1974

Laser Induced Reactions of Propylene and a Study of the Feasibility of the Determination of Sulfuric Acid Aerosol by Laser Induced Infrared Emission.

William Morris Reid
Louisiana State University and Agricultural & Mechanical College

LASER INDUCED REACTIONS OF PROPYLENE

AND

A STUDY OF THE FEASIBILITY OF DETERMINING SULFURIC ACID AEROSOL BY LASER INDUCED INFRARED EMISSION

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of

Doctor of Philosophy

in

The Department of Chemistry

by

William Morris Reid

B.S., Northwestern State College, 1964
M.A., University of Northern Iowa, 1968

DEDICATION

This dissertation is dedicated to those people who, through the years, have provided the inspiration, the encouragement, and the means whereby this end might be realized: to Joe, and most of all to Wanda.

ACKNOWLEDGEMENT

The author wishes to acknowledge the encouragement given him by his major professor, Dr. J.W. Robinson. The assistance provided by Dr. Paul Moses and Paula Boyd is deeply appreciated. Thanks are also due to Dr. Frank Iddings for advice and instruction. Special thanks go to the departmental glass blower, Charles Burlo, for invaluable aid.

The author gratefully acknowledges financial support received from the Dr. Charles E. Coates Memorial Fund of the Louisiana State University Foundation donated by George H. Coates for the preparation of this dissertation.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

Studies involving the analytical potential of laser induced infrared fluorescence for determining various air pollutants have been conducted in our laboratories for several years. The research reported in this dissertation is related to these studies and is divided into two parts. Part I is an investigation of the laser induced reactions of propylene. Part II is an investigation into the feasibility of determining sulfuric acid aerosol by laser induced infrared emission.

PART I

The initial observation that propylene reacted with oxygen in air to form a visible product when irradiated with the CO_2 laser beam during a fluorescence experiment led to a study of this reaction. The reaction was of interest because such a phenomenon could be the source of a direct analytical interference in the determination of propylene in air by the laser method and also because of the relatively low energy of the infrared photons involved and, hence, the uniqueness of the reaction.

Studies of the reaction of propylene with oxygen were conducted with oxygen concentrations of zero, ten, and

thirty volume percent and at laser powers of 20 and 35 watts. The products were characterized by a gas chromatograph-mass spectrometer technique. The results indicated that the reaction was dependent on both oxygen concentration and laser power, with the extent of reaction increasing with increased oxygen concentration and increased laser power.

The effect of increased thermal energy was investigated by heating a propylene-oxygen mixture to 200°C for one hour. There was no discernible reaction and it was concluded that the reaction was a direct result of the absorption of the laser beam by the propylene and not primarily a result of increased thermal energy.

An investigation into the role of acetaldehyde (which was always a major product of the reactions) in the propylene reactions was undertaken. Various acetaldehyde - oxygen, acetaldehyde - propylene, and acetaldehyde - 1,3-butadiene mixtures were investigated and the results led to the conclusion that acetaldehyde was formed as an initial product in the propylene - oxygen reaction and that it further interacted with the laser radiation and decomposed, yielding intermediates which then reacted with propylene to yield the observed products.

It was also concluded that the propylene - oxygen reaction was too slow to be the source of a significant

analytical interference in the determination of propylene in the atmosphere by laser induced infrared fluorescence.

PART II

The recent discovery that the installation of platinum catalytic converters in the exhaust systems of new automobiles results in increased quantities of sulfuric acid aerosol in the exhaust emissions, has brought into focus the need for a reliable, specific method for analyzing for sulfuric acid.

An investigation of the trapping efficiencies of various commonly used trapping agents for sulfuric acid was carried out using a radiotracer technique. These trapping agents were found to be very inefficient for trapping freshly generated sulfuric acid aerosol as generated by platinum catalyst. These results clearly showed a need for a measurement technique which does not require trapping of the sulfuric acid.

A study of the feasibility of determining sulfuric acid aerosol by laser induced infrared emission was carried out. Focussing of a CO_2 laser beam into sulfuric acid aerosol resulted in characteristic infrared emission from the excited sulfuric acid. A characteristic emission band centered at 6.27 microns was monitored, under optimum conditions

and sensitivity data were calculated. The method, as applied with available equipment, was judged to have too little sensitivity for exhaust monitoring, but it was concluded that the method was feasible and with improvements with respect to equipment, could be developed into a useful technique.

I. INTRODUCTION

The work presented in this dissertation is divided into two parts, both of which are related to the use of lasers in analytical chemistry. Part I is concerned with the laser induced chemical reactions of an organic air pollutant (propylene) with oxygen. This study was initiated primarily to determine the analytical effect of such a reaction on the measurement of the concentration of the pollutant in the atmosphere. Part II describes a feasibility study of the use of laser induced infrared emission as a means of determining the concentration of sulfuric acid aerosol in automobile exhaust gases.

During the few years since its discovery, the laser has made important contributions to fundamental research in chemistry, physics, and numerous areas of technology.[1] The uses of lasers in chemistry proceeded more slowly at first than did their uses in other areas of endeavor. In their reviews of 1967, Jones[2] and Haught[3] reported only a few applications of lasers in chemistry. By the end of 1970, the applications of laser techniques in chemistry had produced a literature of staggering proportions. Applications of lasers to spectroscopy have accounted for the bulk of the literature thus far.

There are many reasons for the vast amount of work done with lasers in spectroscopy. The laser is an ideal source for spontaneous scattering experiments and, consequently, the fields of Raman, Brillouin, and Rayleigh scattering have enjoyed a substantial revival.[4] In the field of absorption spectroscopy, tunable lasers have made it possible to obtain high resolution absorption spectra for numerous molecules.[2] Excitation of vibration-rotation energy levels of gaseous molecules by lasers may yield infrared fluorescence spectra which are more easily resolved and assigned than infrared emission from thermal excitation sources.[5-8] The possible uses of these laser techniques are myriad.

One area in which laser induced spectroscopic phenomena may find advantageous application is in air pollution analysis. At the present time, a wide variety of atmospheric pollutants is being monitored at stations throughout the United States.[9] These pollutants are present primarily in the gaseous state and in the part per million or part per billion range. To detect and measure these pollutants usually requires collection at fixed stations over an extended period of time with separation and analysis at some time subsequent to the collection. The total time involved in collection, separation, and analysis may vary

from a few minutes to many hours. All such collection and separation methods are subject to efficiency and interference problems.[10] There is a need for a sensitive, "real-time" method for quantitatively determining atmospheric pollutants over a wide range of concentrations at extended distances. Laser techniques may provide the basis for such methods.

Several techniques which employ lasers for the remote sensing of atmospheric pollutants have been proposed. These techniques include laser beam absorption by the pollutant, Mie scattering, Rayleigh scattering, the Raman effect, and infrared fluorescence. The use of laser induced Mie scattering for the remote sensing of particulates in the atmosphere is well developed.[11] Kildal and Byer have recently evaluated the comparative remote sensing potentials of the Raman effect, infrared fluorescence, and infrared absorption.[12]

In our laboratories, we have been involved in the development of laser induced fluorescence as a remote sensing technique since the original observation of the phenomenon here. This technique obviates collection and separation and offers "real-time" analysis. The technique also offers the theoretical possibility of measuring selected atmospheric pollutants in the part per million range at distances

up to 10 kilometers.[13]

PART I

"LASER INDUCED REACTIONS OF PROPYLENE"

In some of the earlier work with laser induced infrared fluorescence, unexpected chemical reactions were observed to take place during the course of fluorescence experiments. These reactions were unexpected because of the long wavelength (10.6 microns), and hence low energy of the photons constituting the infrared laser train. The energy of a single photon of 10.6 micron radiation is 1.8×10^{-13} erg or 4.3×10^{-21} calories. This energy is sufficient for vibrational excitation but absorption of one or even several such photons would not be expected to increase the molecular energy of most systems to the extent that a reaction would take place.

One of the interesting reactions was that which occurred when a mixture of propylene and air was irradiated with the laser. Propylene absorbs infrared radiation quite strongly at 10.6 microns, and, consequently, provided a basis for interaction with the laser beam. A small amount of condensate appeared on the inside of the glass cell being used in the fluorescence experiment. Investigation

of a previously noted ethylene reaction had indicated the presence of methylene in the reaction and direct cleavage of the carbon-carbon double bond by absorption of the laser beam was concluded.[14] The propylene reaction was different in that it did not occur in the absence of oxygen, negating the possibility of a direct cleavage of any bond in the propylene by absorption of the laser beam. A study of the laser induced reaction of propylene was conducted for three basic reasons. First, the loss of propylene through reaction during a remote sensing experiment for the atmospheric pollutant could be the cause of a direct analytical interference. Second, laser induced reactions using relatively low power continuous infrared lasers are unique, with none reported other than from these laboratories. Third, the identification of the reactive intermediate and its source could shed some light on the mechanism of such reactions and could thus be a very significant contribution to laser induced chemistry.

Gas phase chemical reactions induced by absorption of infrared laser radiation have been studied by others.[15-20] These studies, however, were under very different conditions from those employed in this study. All of the reported reactions were induced either by Q-switched lasers or by the focussed beam of a continuous laser. Each of these types of

laser operation yields very high power densities in the beam and molecules subjected to the radiation are essentially pyrolyzed. The laser used in this investigation was a relatively low power carbon dioxide laser. It was neither focussed nor Q-switched. The principal lasing line was at 10.6 microns and the maximum power output was 35 watts when operating in the continuous mode.

Although the initially observed propylene reaction was with air, the products were all either hydrocarbons or oxygenated hydrocarbons and, consequently, subsequent studies were carried out with propylene/oxygen systems. Studies were performed at oxygen concentrations of zero, ten, and thirty volume percent and at laser powers of 35 watts and 20 watts.

The results indicated that the extent of the reaction was very dependent on the oxygen concentration. No reaction occurred when oxygen was scrupulously excluded. With oxygen present, reaction occurred producing essentially the same products and product distributions with the two oxygen concentrations employed. The extent of reaction however increased with increased oxygen concentration.

Results also indicated a dependence of the reaction on laser power. The extent of reaction markedly increased with increased laser power from 20 watts to 35 watts.

Many products were formed after irradiation with a laser power of 35 watts that were not detected when irradiated with the laser power at 20 watts. All products detected after irradiations with the laser operating at 20 watts were also detected when the power was at 35 watts, but there was a wide variation in the concentrations.

The product distributions after irradiations with laser powers of 20 watts and 35 watts indicated that acetaldehyde was formed as a primary product and then it chemically reacted in various modes. Acetaldehyde also was found to absorb infrared radiation strongly at 10.6 microns and irradiations of acetaldehyde alone and mixed with oxygen yielded many of the same products as in the propylene reaction. Acetaldehyde is known to decompose thermally through a free radical mechanism at temperatures as low as $430^{o}C$[21] giving much the same product distribution as noted in the laser experiment. It should be pointed out however, that the measured temperature inside the reaction cell never approached such a high temperature.

It was questioned whether the reaction was the result of the thermal energy increase accompanying the laser beam absorption. The temperature increase inside the reaction cell was very small. At a distance of 5 millimeters from the outer edge of the laser beam, the temperature

never rose above 57°C during the course of an experiment. There is, of course, the question concerning the temperature inside the laser beam itself. The temperature inside the laser beam, although impossible to measure, is probably higher than that outside the beam. The thermal infrared emission observed in laser induced fluorescence experiments however, is low, indicating relatively little heating.[22] Comparative studies in the absence of the laser radiation were conducted at 200°C to compensate for any discrepancy between the measured temperature and the temperature in the beam.

Results showed that there was no measurable reaction at this temperature, thus indicating that the laser induced reaction was not primarily thermal in nature.

It has been shown that the thermal decomposition of acetaldehyde is catalyzed by oxygen[23] and that, for other systems, absorption of radiation from a laser by a molecule can also lower the energy of activation for a given reaction.[24]

It was concluded that, because of the time scale involved, the reaction was not fast enough to constitute a direct interference in the determination of propylene as an air pollutant. It was also concluded that the reaction was not primarily the result of increased thermal energy but was the result of a direct interaction of the propylene with

the laser beam. The reaction appears to be a result of the interaction of an excited species of propylene with oxygen to produce acetaldehyde as a primary product. The acetaldehyde then further reacted under the influence of the laser beam to give the other observed products.

PART 2

"A STUDY OF THE FEASIBILITY OF DETERMINING SULFURIC ACID AEROSOL BY LASER INDUCED INFRARED EMISSION"

An atmospheric pollutant that has been receiving an increasing amount of attention recently is sulfuric acid aerosol. Sulfuric acid aerosol is present in the atmosphere primarily as a result of the burning of fuels which contain sulfur. The major sulfur-containing product of such combustion is sulfur dioxide. Sulfur dioxide enters the atmosphere, as a result of combustion, at a world-wide rate of about 150 million tons per year.[25] The ultimate fate of this sulfur dioxide is either catalytic or photochemical oxidation to sulfate. Much of this sulfate is in the form of sulfuric acid.[26] There are wide-spread disagreements in the literature over the rate of the oxidation of the sulfur dioxide in the atmosphere.[27,28] The rate varies considerably with atmospheric conditions but essentially complete

oxidation appears to involve several hours.

Sulfuric acid aerosol as an atmospheric pollutant has received little attention until recently. This is because the sulfur dioxide from which it is formed has been rather well dispersed through the atmosphere before the oxidation to sulfate takes place. Consequently, no locally significant concentrations of sulfuric acid aerosol have been encountered.

The most important consideration with respect to sulfuric acid aerosol as an air pollutant is undoubtedly the health effects on human beings. Unfortunately, these health effects are not well defined. Indications are, however, that chronic exposure to sulfuric acid aerosol can produce serious pulmonary impairment and can suppress responses of the central nervous system.[29]

In an effort to protect the public health, the Congress, in the Clean Air Act of 1970, has mandated a drastic reduction in automotive emissions from new vehicles beginning with the 1975 model year. The automotive industry has responded to this demand by developing a platinum catalytic converter which, when placed in the automotive exhaust system, very efficiently converts unburned hydrocarbons and carbon monoxide to carbon dioxide and water. However, the converter also catalyzes the oxidation of

sulfur dioxide to sulfur trioxide which then reacts with water to form sulfuric acid aerosol.

The significance of the automobile as a sulfuric acid pollution source has now become great. The emission of sulfuric acid from the tail pipes of automobiles equipped with catalytic converters will obviously occur at street level and locally high concentrations of sulfuric acid in the air are likely, especially in metropolitan areas. The Environmental Protection Agency estimates that the range of sulfate emission values for catalyst equipped cars using 0.03% sulfur fuel is 0.005 to 0.3 grams per mile.[30] This corresponds to a range of from 50 grams to 3 kilograms for a car being driven 10,000 miles in a year.

In order to control pollution of the atmosphere by sulfuric acid aerosol from catalyst equipped cars, an accurate, reliable method for measuring the sulfuric acid is needed. The Environmental Protection Agency has stated that there is no generally accepted measurement procedure and that emission of sulfuric acid from catalyst cars cannot be quantified with a high degree of confidence (the above-given values were estimates based on preliminary data).[30] All of the methods currently in use involve collection of the sulfuric acid in some trapping medium, such as fluoropore filters or water, and subsequent determination

as either sulfate or as an acid.[31-33] Obviously other acids and sulfates trapped may constitute interferences. Even under optimum conditions, these methods are plagued with the inherent inaccuracies and problems associated with collection and separation techniques.

There is considerable evidence that freshly generated sulfuric acid is difficult to trap. In the commercial catalytic process for production of sulfuric acid (which is similar in many respects to a platinum catalytic converter system) considerable effort was put into the problem of collecting in water the sulfuric acid produced. However, because of the inefficiency of the scrubbing agent, it was finally abandoned and concentrated sulfuric acid was used.[34] If these scrubbing data are still valid in the automobile exhaust, then currently used scrubbing methods will be ineffective and lead to erroneously low analytical answers.

The present study was undertaken to test the trapping efficiencies of various trapping agents for freshly generated sulfuric acid, as present in the exhausts of catalyst equipped cars, and to investigate the feasibility of using laser induced infrared emission as a method for determining sulfuric acid aerosol in automotive exhausts. Such a method of analysis would be rapid, simple, specific,

and would not be subject to errors arising from sampling problems since no pretreatment or scrubbing of the exhaust would be necessary.

The sulfuric acid trapping agents studied were fluoropore filter material (0.5 micron pore size), water, sodium carbonate solution, and sodium hydroxide solution. The analytical technique employed in this investigation was a radio-tracer technique utilizing liquid scintillation counting as the measurement method. Sulfur dioxide was generated by addition of hydrochloric acid to an aqueous solution of ordinary sodium sulfite and sodium sulfite labelled with sulfur-35. Sulfur-35 is a beta-emitting radioactive isotope of sulfur. The sulfur dioxide was converted to sulfuric acid by passing it over heated platinum catalyst with air saturated with water vapor. The effluent from the platinum catalyst was then passed sequentially through a fluoropore filter, sodium tetrachloromercurate(II) solution, water, sodium carbonate solution, and sodium hydroxide solution. Results indicated that the fluoropore filter and the water were very poor traps (the sodium tetrachloromercurate(II) trap was for unoxidized sulfur dioxide). Approximately 90% of the sulfuric acid passed through both the filter and the water. Approximately 40% also passed through the sodium carbonate solution to be trapped in the

sodium hydroxide trap.

These data indicated that freshly generated sulfuric acid is indeed difficult to trap and that currently used scrubbing techniques for sulfuric acid in automobile exhausts are quite probably inefficient. Such inefficiency obviously will lead to erroneously low analytical answers. These results point to the need for a reliable method for analysis of sulfuric acid aerosol in automobile exhausts which does not involve trapping of the sulfuric acid.

Sulfuric acid absorbs infrared radiation strongly at 10.6 microns, thus providing a basis for its interaction with the beam from a carbon dioxide laser whose principal lasing line is 10.6 microns. The carbon dioxide laser used in this study was the same as that used in the propylene study. However, the maximum power output had diminished to 30 watts for unknown reasons. Concentrated sulfuric acid was aspirated through the focal point of the focussed beam of the laser and a portion of the radiation emitted by the excited acid was collected and focussed onto the entrance slit of a monochromator-detector system. The laser induced emission spectrum of sulfuric acid was recorded and a characteristic emission band was selected to be monitored for quantitative studies. The sulfuric acid emission intensity was measuted at various aspirator gas flow rates at laser

powers varying from 10 to 30 watts.

The results showed that the emission intensity was dependent on both aspirator gas flow rate and laser power. At the optimum flow rate of 1 liter per minute, maximum signal was obtained for all laser powers and both 25 and 30 watt laser powers gave the same signal intensity. At higher flow rates, there was an essentially linear relationship between signal intensity and laser power.

The calculated sensitivity of 2×10^{-6} grams per cubic centimeter under optimum conditions for our system was determined to be insufficient for monitoring automobile exhausts for sulfuric acid aerosol. However, it was concluded that the method is feasible and with improvements with respect to maximum laser power and the optical system a promising technique may be developed.

II. EQUIPMENT AND REAGENTS

The following equipment and reagents were used.

PART I

A. Infrared Laser

A Perkin-Elmer, Model 6200, molecular carbon dioxide gas laser was used for all laser induced reaction studies. The laser produced a maximum of 35 watts of continuous power at about 10.6 microns in a beam approximately one centimeter in diameter.

B. Alignment Laser

A Metrologic Instruments, Model 210, helium-neon laser was used at various times to aid in the alignment of the components of the optical system.

C. Power Meter

A Coherent Radiation, Model 201, power meter was used in all measurements of laser output power. The power meter was capable of measuring infrared laser radiation up to 100 watts.

D. Reaction Cells

1. Laser Induced Reaction Studies

All of the reaction cells used in this study were

cylindrical and made from Pyrex glass. In the construction of these cells, ¼ inch stems were provided for introduction of gases and one inch diameter Irtran-2 (Eastman Kodak) windows were used as laser beam entrance and exit windows. Irtran-2 material transmits infrared radiation with wavelengths shorter than 15 microns.

The first reaction cell used was relatively large, having an overall length of 54 centimeters and a diameter of 6.7 centimeters. Standard taper 29/42 ground glass joints constituted the ends of the cell and the Irtran-2 windows were sealed to these joints with an epoxy cement. This cell was quite inefficient with respect to product yield due to its large volume relative to the volume occupied by the laser beam and product analysis was quite difficult. The laser beam occupied only about 2% of the total volume of the cell.

This cell was replaced by a smaller cell of similar construction which was 22 centimeters long and 5 centimeters in diameter. The laser beam occupied approximately 4% of the volume of the new cell. This cell, however, suffered from the same problem as the previous cell.

Another, still smaller, cell was built which gave good product yields. This cell was 3 centimeters in diameter and 18 centimeters long. The laser beam occupied

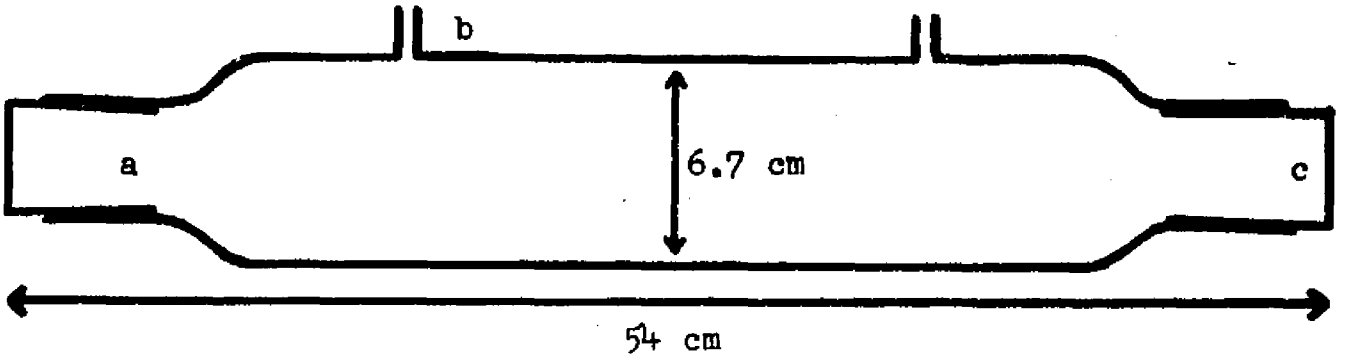
about 11% of the total cell volume with this design.

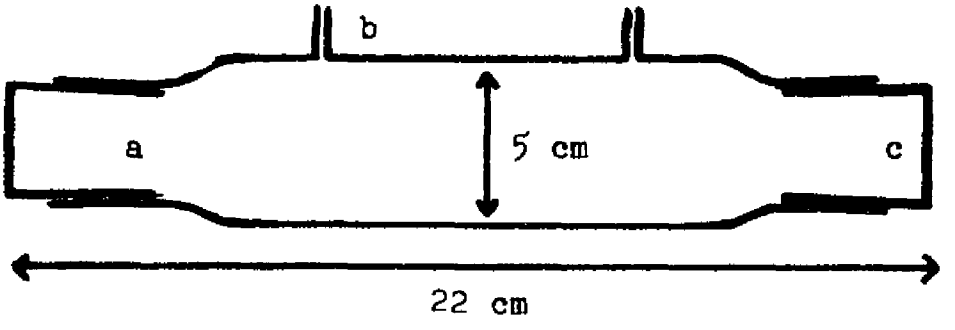
The physical dimensions of these cells are shown in Figure 1.

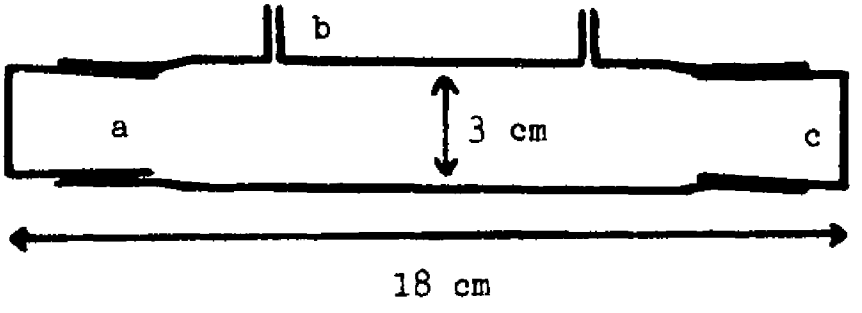
In efforts directed towards elimination of oxygen as a contaminant in the 100% propylene reaction study, a new cell was designed and built. This cell was similar to those previously described except that the Irtran-2 windows were held in place by O-ring joints compressed by spring clips. This cell was 2.6 centimeters in diameter and 18 centimeters in length. The design of this cell is shown in Figure 2.

2. Thermal Studies

In a study undertaken to determine the heating effect of absorption of the laser beam during a reaction, a cell was used which incorporated a thermometer in its construction. The cell was identical to the 18 centimeter cell in Figure 1 except that a third stem utilizing a 10/30 standard taper ground glass joint was provided to hold a thermometer in the cell. The cell was so constructed that the bulb of the thermometer was a calculated 5 millimeters from the outer edge of the laser beam. The cell is illustrated in Figure 3.





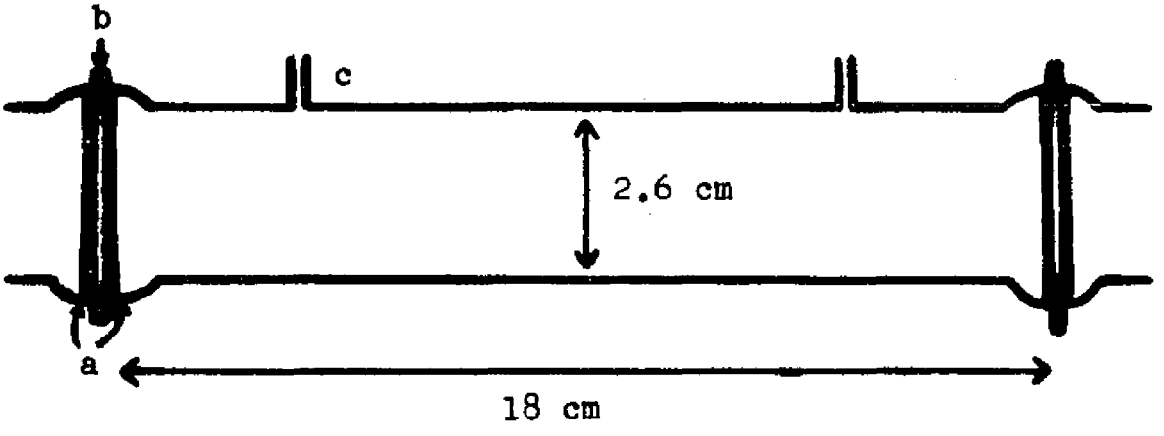


a. 29/42 standard taper ground glass joint

b. Pyrex stem, ¼ inch diameter, 3/4 inch length

c. Irtran-2 window, 1 inch diameter, 1 mm thickness

Figure 1. GLASS REACTION CELLS

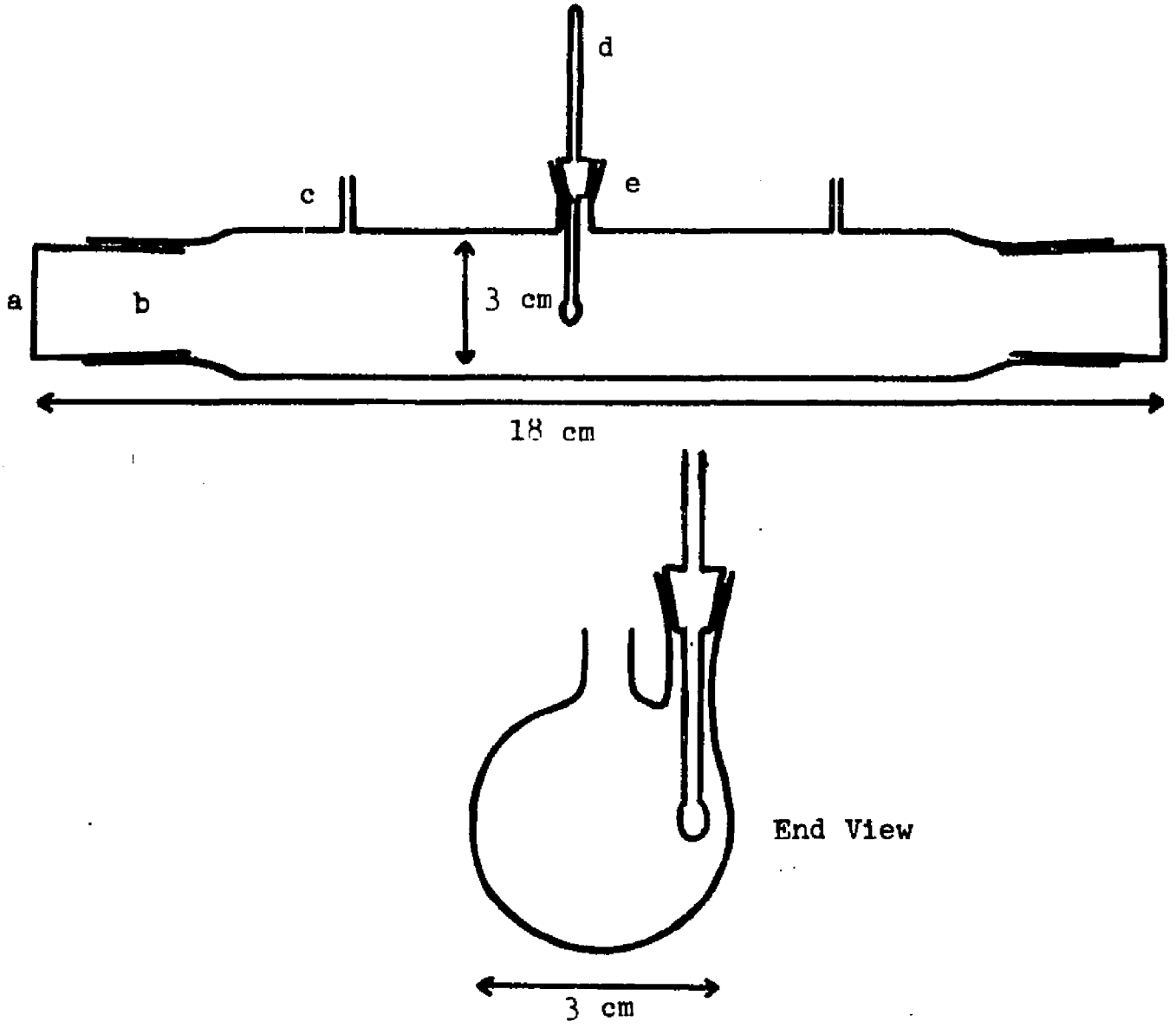


a. O-rings, rubber, 1 inch diameter

b. Irtran-2 window, 1 inch diameter, 1 mm thickness

c. Pyrex stems, ¼ inch diameter, 3/4 inch length

Figure 2. O-RING REACTION CELL



a. Irtran-2 window, 1 inch diameter, 1 mm thickness

b. 29/42 standard taper ground glass joints

c. Pyrex stems, ¼ inch diameter, 3/4 inch length

d. Thermometer

e. 10/30 standard taper ground glass joint

Figure 3. THERMAL STUDY REACTION CELL

The cell employed for the investigation of a possible thermally induced reaction of propylene was the same as the 18 centimeter cell shown in Figure 1.

E. F and M Gas Chromatograph

Initial studies of the products of the laser induced reaction were carried out with an F and M Scientific Corporation Research Chromatograph, Model 810. The instrument was temperature programmable and utilized dual columns and dual thermal conductivity detectors.

F. Gas Chromatograph - Mass Spectrometer Combination

The bulk of the analyses of reaction products was carried out with a Perkin-Elmer, Model 990, gas chromatograph interfaced with a Hitachi-Perkin-Elmer RMS-4 Mass Spectrometer. The chromatograph utilized a flame ionization detector and the G.C.-M.S. interface included a stream splitter so that part of the column effluent could be diverted to the mass spectrometer.

G. Gas Chromatograph Columns

The columns used in the majority of the analyses were packed with Porapak S packing material. Porapak S is composed of highly cross-linked, porous polymer beads and is particularly good for separation of very volatile compounds. Two columns, 8 feet and 20 feet in length and

1/8 inch in diameter.

H. Infrared Spectrophotometer

A Beckman Infrachord infrared spectrophotometer was used in some of the early work with liquid reaction products.

I. Nuclear Magnetic Resonance Spectrophotometers

Varian, Models A-60A and HA-100A, NMR Spectrometers were used in characterization of liquid reaction products of early work.

J. Gas Syringe

Injection of gaseous samples for gas chromatographic analysis was accomplished with a Precision Sampling Pressure Lok Syringe. The maximum volume was 10 milliliters with 0.1 milliliter graduations.

K. Reagents

1. Propylene -- Matheson, 99.9% pure. Gas chromatographic analysis showed the only detectable impurity to be 0.04% trans-2-butene.
2. Oxygen -- Matheson, chemically pure.
3. Carbon dioxide -- Matheson, chemically pure.
4. Carbon tetrachloride -- Malinckrodt, analytical

reagent

5. Acetaldehyde -- Matheson, Coleman, Bell - b.p. 20-22°C.

6. Copper turnings -- Baker and Adamson.

7. Calcium sulfate -- W.A. Hammond Drierite.

PART II

A. Oven

A Hevi Duty Electric Company Multiple Unit tube-type oven was used to heat the platinum catalyst to 400°C.

B. Thermocouple

An Edmund Scientific Company thermocouple, capable of measuring temperatures from 0°C to 1370°C was used to indicate the temperature of the platinum catalyst.

C. Ultraviolet Spectrophotometer

A Beckman DB-G ultraviolet-visible spectrophotometer was used in colorimetrically determining the sulfur dioxide concentration in the sodium tetrachloromercurate(II) solution employed in the West-Gaeke test.

D. Filter Material

0.5 micron pore size fluoropore filters having a ciameter of 25 millimeters were obtained from the Millipore Corporation and used as one of the types of trapping agents for sulfuric acid.

E. Flow Meters

A Matheson Company flow meter fitted with a Model 601 tube was used to regulate the air flow in the trapping

studies.

A Brooks Rotameter Company flow meter fitted with a Model 3-65B tube was used to regulate the flow of nitrogen through the aspirator in the generation of sulfuric acid aerosol.

F. Liquid Scintillation System

A Beckman Instruments LS-250 Liquid Scintillation System was used to measure the activity of the various sulfur-35 containing solutions in the trapping studies.

G. Infrared Laser

A Perkin-Elmer Model 6200 Molecular Carbon Dioxide Laser was used to induce infrared emission in sulfuric acid aerosol. The laser produced a maximum of 30 watts of continuous power at 10.6 microns in a beam approximately one centimeter in diameter. (The maximum power output of the laser, as measured by two different power meters, had declined from the 35 watt maximum of previous experiments.)

H. Mirrors

1. Focussing Mirror

A concave, front surface aluminum mirror, having a 7.5 centimeter diameter and a 20 centimeter focal length, was used to focus the laser beam to a spot 1 millimeter in

diameter.

2. Collecting Mirror

A concave, front surface mirror, having a 10 centimeterdiameter and a 20 centimeter focal length was used to collect a portion of the radiation emitted from the excited sulfuric acid and to focus it on the entrance slit of the monochromator.

I. Aspirator

A Beckman Flame Photometer atomizer-burner was used to provide sulfuric acid aerosol for the laser induced emission studies. Nitrogen was used as the aspirator gas. The fuel port of the atomizer was left open.

J. Monochromators

1. Thermal Emission Study

In the experiment in which the thermal emission spectrum of concentrated sulfuric acid was obtained, a Beckman Instruments Model IR-10 infrared spectrophotometer was used. The equipment was operated in the single beam mode and was equipped with a thermocouple detector.

2. Laser Induced Emission Study

A McPherson Model 218, 0.3 meter monochromator fitted with a 75 groove per millimeter grating, giving a utilization range of 0.105 microns to 16.00 microns, blazed

for 8 microns, was used in the laser work. The monochromator was fitted with an order selecting filter system and a pyroelectric detector.

K. Filter Assembly

A McPherson Model 607 filter assembly was used as an order selector. Four selectable positions were available on the assembly. Three of these positions were occupied by different filters. The fourth position was open. The transmission curves of the three filters are shown in Figure 4.

L. Detector

A Barnes Engineering Model 662 Triglycene Sulfate Pyroelectric Detector was used in all experiments except when the Beckman IR-10 spectrophotometer was used to record the thermal emission spectrum of sulfuric acid. The detector was mounted directly on the McPherson monochromator. The electronic circuitry, mounting, and operational details have been described.[35]

M. Signal Modulators

1. Thermal Emission Study

The Beckman IR-10 infrared spectrophotometer was operated in its original optical configuration with the ra-

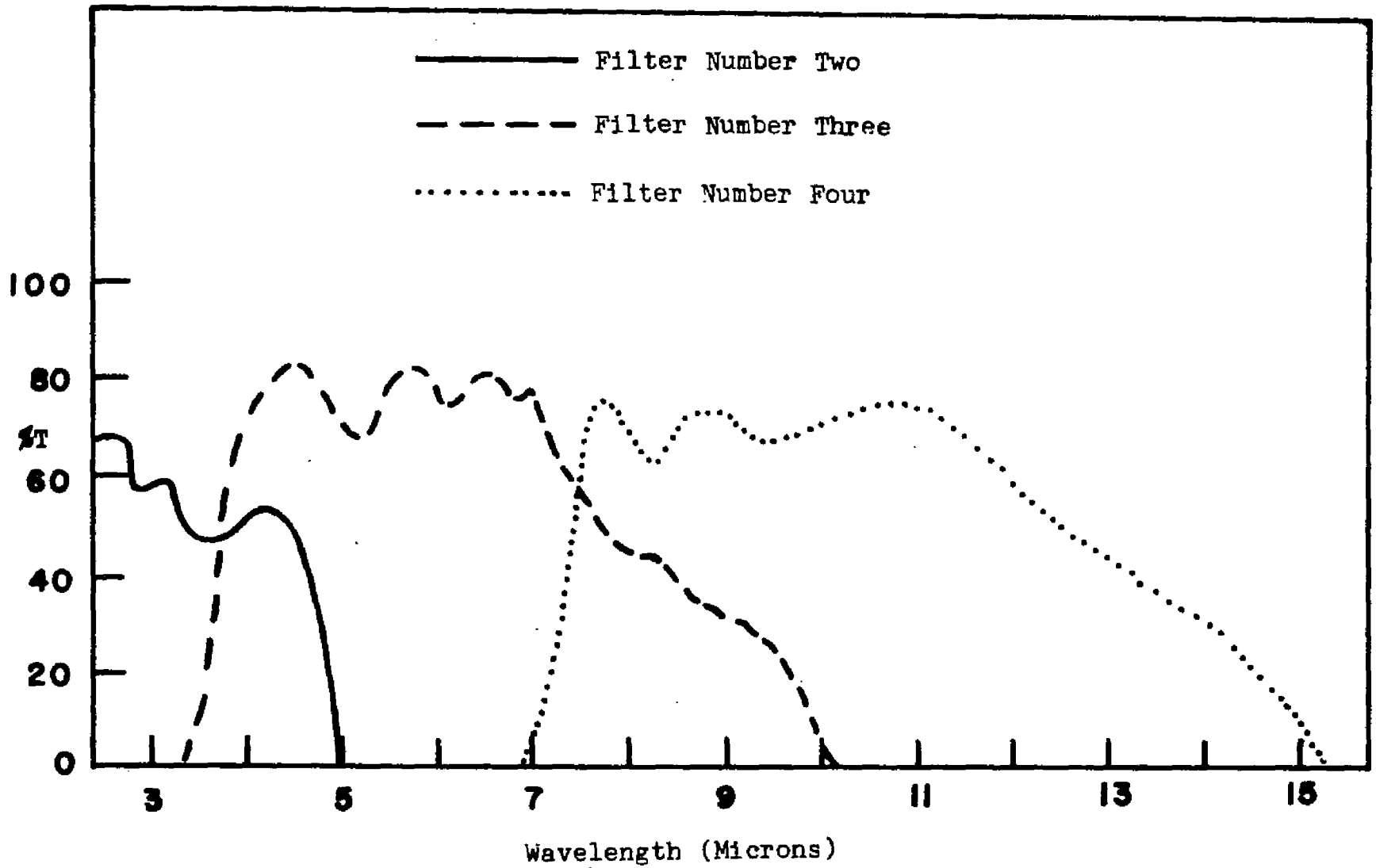


Figure 4. TRANSMISSION CURVES OF INFRARED BANDPASS FILTERS

diation being modulated at 10 Hertz by a mechanical chopper just prior to its passage through the entrance slit.

2. Laser Induced Emission Study

In all of the laser induced emission experiments, a Princeton Applied Research Model 125 mechanical chopper was used to modulate the infrared emission. The chopper was operated at 13 Hertz.

N. Amplifier and Preamplifier

A Princeton Applied Research Model 124 lock-in amplifier and Model 116 differential preamplifier were used to amplify the detector signals.

O. Recorder

A Texas Instruments Servo-Riter strip-chart recorder was used to display the amplified signals from the amplifier.

P. Power Meter

A Coherent Radiation Model 210 power meter capable of measuring laser powers up to 100 watts was used to monitor the output power of the laser. The surface area of the meter sensing element was 2.9 cm^2, giving a measuring capacity of approximately 35 watts per cm^2. The maximum permissible power density was 200 watts per cm^2.

Q. Infrared Spectrophotometer

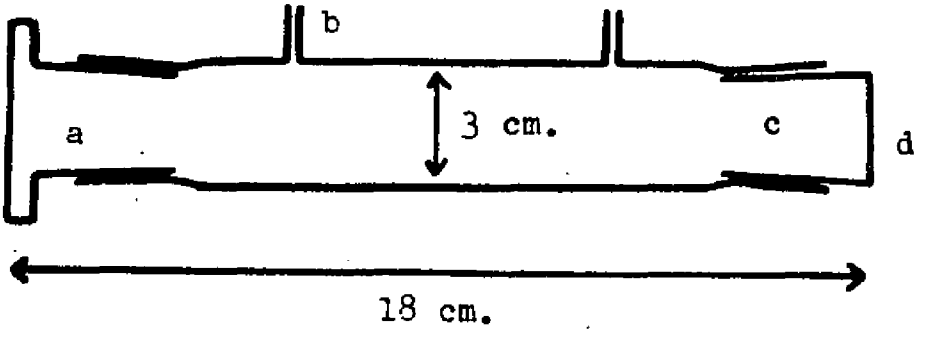
A Beckman Infrachord infrared spectrophotometer was used to obtain the absorption spectrum of concentrated sulfuric acid. The sulfuric acid was used as a thin film between silver chloride plates.

R. Gas Cell

A small pyrex glass cell (Figure 5) was used to obtain the thermal emission spectrum of sulfuric acid. A glass stopper was used in one end of the cell and a 1 inch diameter Irtran-2 (Eastman-Kodak) window was used as the exit for the radiation from the cell.

S. Reagents

1. Platinum catalyst -- catalyst obtained from General Motors Corporation.
2. Sodium carbonate -- Malinckrodt, Analytical Reagent.
3. Sodium hydroxide -- Matheson, Coleman, Bell, A.R.
4. Mercury(II) chloride -- Merck and Co., Inc., A.R.
5. Sodium chloride -- Fisher Scientific Co., A.R.
6. Formaldehyde -- 37% - Malinckrodt, A.R.
7. p-Rosaniline hydrochloride -- Chem Tech Laboratories
8. Hydrochloric acid -- Malinckrodt, 37%.
9. Sodium sulfite -- anhydrous, Malinckrodt.
10. Labelled sodium sulfite -- New England Nuclear Corp.



a. Glass stopper

b. Pyrex stems, ¼ inch diameter, 3/4 inch length

c. 29/42 standard taper ground glass joints

d. Irtran-2 window, 1 inch diameter, 1mm thickness

Figure 5. GAS CELL FOR SULFURIC ACID THERMAL EMISSION STUDY

11. 2,5-diphenyloxazole -- J.T. Baker, scintillation grade.
12. 1,4-di-2(5-phenyl-oxazolyl)-benzene -- Atomic Accessories, Inc.
13. Naphthalene -- Malinckrodt, A.R.
14. p-Dioxane -- Matheson, Coleman, Bell, A.R.
15. Nitrogen -- Matheson, 99.9% pure.
16. Sulfuric acid -- Malinckrodt, 96%, A.R.

III. EXPERIMENTAL PROCEDURES, RESULTS, AND DISCUSSION

PART I

Reactions of the following gaseous systems, with concentrations expressed as volume percents, were studied: 100% propylene, 90% propylene - 10% oxygen, 80% propylene - 20% oxygen, 70% propylene - 30% oxygen, 100% acetaldehyde, 90% acetaldehyde - 10% oxygen, 90% propylene - 10% acetaldehyde, 89% propylene - 10% acetaldehyde - 1% oxygen, 90% propane - 5% acetaldehyde - 5% oxygen, 80% butadiene - 20% oxygen, 35% butadiene - 55% acetaldehyde - 10% oxygen.

A. Preparation of Gas Mixtures

Initially, the propylene - oxygen systems were mixed by means of calibrated flow meters. In the early work, irradiations with the laser beam were carried out with the gas mixture flowing through the cell. In later work, the gases were allowed to flow through the cell for several minutes, the flow was stopped, and the cell was then sealed. On several occassions, the cell stems were fitted with Swagelok unions and septa and the desired quantities of gases were injected by means of a gas-tight sytinge into the evacuated cell. The mixtures involving acetaldehyde were all produced by injections into evacuated

cells.

B. Operational Characteristics of the Perkin-Elmer Laser

The Perkin-Elmer laser was capable of a peak power output of about 45 watts when first turned on. However, heating brought about by the plasma caused a rapid decrease in power with time. This change was caused by a decrease in the efficiency of depopulation of the lower energy lasing level of the carbon dioxide molecules and also by mirror geometry changes. After temperature stabilization, mirror adjustments produced a maximum sustainable power of 35 watts. Adjustments of the current through the plasma provided the capability of operating the laser at selected lower powers.

The beam produced by the laser was essentially circular with a diameter of approximately one centimeter. The power distribution in the beam, however, was not even at any given instant. Hot spots caused by moding within the beam were seen on asbestos placed in its path. Various mode patterns were seen, which continuously and rapidly changed. These shifting patterns produced an even distribution throughout the beam over a period of a few seconds.

The laser operates principally on the 10.6 micron band, but it has been observed to operate simultaneously at other wavelengths between 9.2 and 10.8 microns with varying

intensities (Figure 6). Propylene absorbs infrared radiation rather strongly in a broad band extending through this range (Figure 7).

C. Qualitative Analysis of Reaction Products

Qualitative analysis of product mixtures was accomplished with the gas chromatograph-mass spectrometer combination. For analysis of the initially observed liquid reaction products, the OV-1 column was used for separation of the components. For all other analyses, either the 8 foot or the 20 foot Porapak column was used, depending upon the resolution required. The column effluent was divided by the "splitter", with part of it being directed to the ionization chamber of the mass spectrometer and part of it being directed to the flame detector of the gas chromatograph.

Information concerning the structures of the components was obtained from both gas chromatographic data and mass spectral data. Authentic samples of suspected compounds, when available, were analyzed under the same conditions as the unknown and their retention times and mass spectra correlated.

Mass spectral correlations were based on characteristic cracking patterns of the molecules concerned. The parent mass, masses of fragment ions, isotopic clusters,

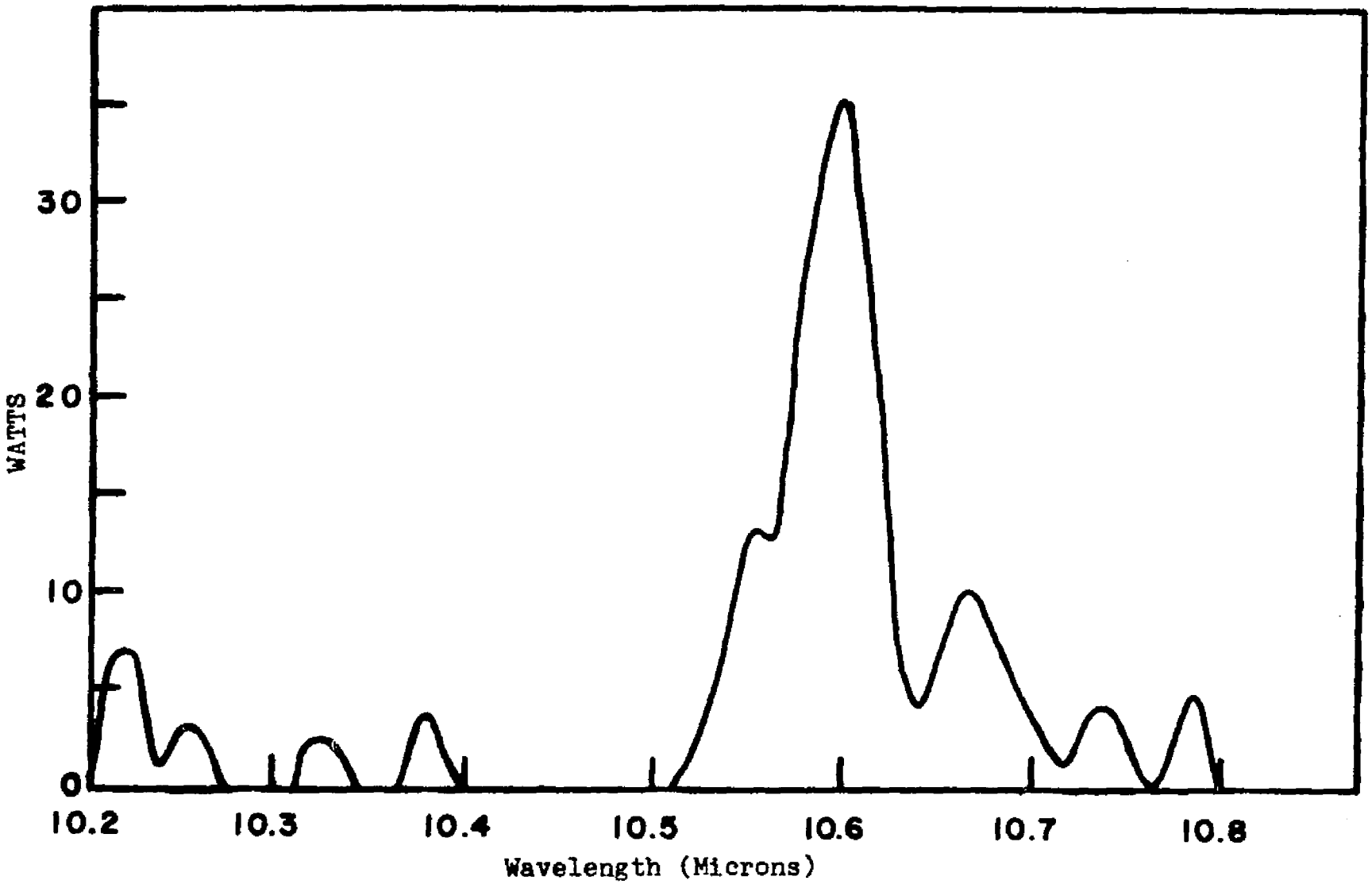


Figure 6. LASING WAVELENGTHS OF PERKIN-ELMER LASER

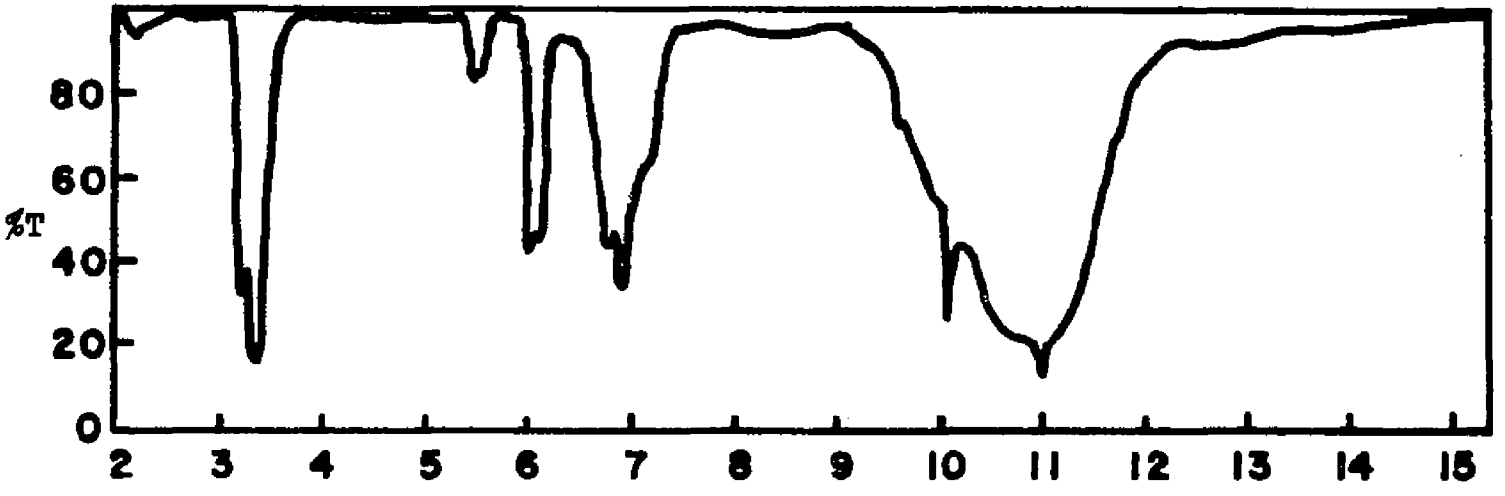


Figure 7. INFRARED ABSORPTION SPECTRUM FOR PROPYLENE

and the relative intensities of the signals from the various ions were used in deducing an appropriate structure for an unknown component and in making correlations with spectra from authentic samples. The cracking patterns of authentic samples were found to compare well with those contained in the Atlas of Mass Spectral Data[36], consequently, when authentic samples were not readily available, confirmations of structure were based upon comparison with spectra in this work.

The retention times of the identified products are shown in Table 1. Experimental mass spectra, reference spectra from the Atlas of Mass Spectral Data, and spectra from authentic samples are given in Table 2.

In some of the early work, small amounts of liquid products were formed and mass spectral analysis showed them to be complex mixtures of relatively high molecular weight, long chain, saturated hydrocarbons. Infrared spectroscopy and nuclear magnetic resonance spectroscopy were used to help further determine structural information on these components.

D. Quantitative Analysis of Reaction Products

Quantitative analyses of the components of the product mixture were carried out with the Perkin-Elmer 990

TABLE 1

Retention Times of Common Reaction Products

Component	Retention Time (Minutes) 8 foot column[1]	20 foot column[2]
Methane	1	2.5
Carbon dioxide	1.5	4
Ethylene	2	5
Ethane	-	6
Water	5	8
Propylene	7	11
Propane	8	13
Formaldehyde	10	14
Acetaldehyde	14	18
1-Butene	16	21
trans-2-Butene	17	22
cis-2-Butene	-	23
Propylene oxide	21	27
Propanal	22	28
Acetone	24	29
Hexadiene	31	39
4-methyl-1,3-Dioxolane	35	42

[1]Program of 70°-200° C at 4°C/minute. Carrier gas flow rate of 25 ml./minute.

[2]Program of 90°-225° C at 4°C/minute. Carrier gas flow rate of 25 ml./minute.

TABLE 2

Mass Spectral Data

The experimental spectra presented in this table were used, along with gas chromatographic retention times, as the basis for qualitative identifications. Reference spectra were obtained from the Atlas of Mass Spectral Data,[36] and authentic samples. The quantity listed as intensity was the height in centimeters of the most abundant peak in the spectrum. Peaks not accurately measurable due to the weakness of the spectra were not listed.

1. Methane

Intensity - 92

m/e	Relative Intensity		
	Experimental	Reference	Authentic
12	1	1	1
13	3	3	4
14	9	8	9
15	81	79	79
16	100	100	100

2. Ethylene

Intensity - 8

m/e	Relative Intensity		
	Experimental	Reference	Authentic
14	3	2	
24	3	3	
25	9	8	
26	55	53	
27	61	62	
28	100	100	
29	2	2	

3. Ethane

Intensity - 7

m/e	Relative Intensity		
	Experimental	Reference	Authentic
14	1	1	2
15	2	2	3
25	2	2	3
26	17	18	18
27	26	29	27
28	100	100	100
29	21	24	24
30	26	30	28

4. Formaldehyde

Intensity - 129

m/e	Relative Intensity		
	Experimental	Reference	Authentic
12	1	3	1
13	1	4	1
14	1	4	1
16	1	2	2
28	29	31	26
29	100	100	100
30	86	88	88
31	2	3	2

5. Methanol

Intensity - 3

m/e	Relative Intensity		
	Experimental	Reference	Authentic
28	10	9	6
29	71	70	65
30	8	8	5
31	100	100	100
32	67	66	70

6. Carbon Dioxide

Intensity - 88

m/e	Relative Intensity		
	Experimental	Reference	Authentic
16	4	6	6
22	1	1	1
28	6	7	6
44	100	100	100
45	1	1	1

7. Propane

Intensity - 2

m/e	Relative Intensity		
	Experimental	Reference	Authentic
26	6	5	6
27	31	32	34
28	43	60	50
29	100	100	100
38	6	5	5
39	16	18	15
41	16	13	14
42	8	6	6
43	28	23	27
44	29	29	31

8. Acetaldehyde

Intensity - 24

m/e	Relative Intensity		
	Experimental	Reference	Authentic
12	2	1	1
13	2	3	3
14	12	10	11
15	39	32	33
16	6	5	6
25	3	3	3
26	6	5	7
27	5	3	5
29	100	100	100
30	2	1	1
41	4	5	6
42	11	12	12
43	40	42	41
44	71	77	73
45	2	2	2

9. Ethanol

Intensity - 3

m/e	Relative Intensity		
	Experimental	Reference	Authentic
15	6	5	4
27	20	18	19
28	6	4	5
29	12	15	16
31	100	100	100
43	8	11	6
45	45	49	52
46	20	23	21

10. 1-Butene

Intensity - 100

m/e	Relative Intensity		
	Experimental	Reference	Authentic
14	1	1	1
15	2	1	1
26	7	5	7
27	23	20	24
28	28	23	28
29	14	11	13
39	32	30	35
40	7	6	7
41	100	100	100
42	4	4	3

10. 1-Butene -- (continued)

m/e	Relative Intensity		
	Experimental	Reference	Authentic
53	6	6	4
55	19	22	22
56	46	47	50
57	2	2	2

11. 2-Butene

Intensity - 20

m/e	Relative Intensity		
	Experimental	Reference	Authentic
26	5	7	8
27	19	22	27
29	13	15	17
39	29	33	36
40	5	6	7
41	100	100	100
42	3	3	4
50	5	7	7
53	8	9	10
54	3	4	5
55	28	27	30
56	64	55	66
57	1	2	3

12. Acrolein

Intensity - 2

m/e	Relative Intensity		
	Experimental	Reference	Authentic
26	52	48	
27	100	100	
28	50	51	
29	34	42	
55	51	63	
56	75	82	

13. Propanal

Intensity - 4

m/e	Relative Intensity		
	Experimental	Reference	Authentic
26	12	10	13
27	42	35	42
28	58	62	58
29	100	100	100
30	6	6	5
31	6	4	7
57	15	19	17
58	62	64	61

14. Acetone

Intensity - 4

m/e	Relative Intensity		
	Experimental	Reference	Authentic
15	21	-	13
27	4	6	4
29	5	4	4
42	8	7	6
43	100	100	100
58	32	34	35

15. Propylene Oxide

Intensity - 9

m/e	Relative Intensity		
	Experimental	Reference	Authentic
14	6	12	
15	26	27	
26	36	40	
27	66	63	
28	100	100	
29	73	68	
30	9	9	
31	35	32	
39	6	6	
43	33	32	
57	7	4	
58	61	43	
59	3	2	

16. Allyl Alcohol

Intensity - 4

m/e	Relative Intensity		
	Experimental	Reference	Authentic
15	7	6	
26	16	21	
27	42	45	
28	19	26	
29	49	80	
30	11	24	
31	46	60	
39	23	40	
43	19	6	
57	100	100	
58	28	27	

17. Acetic Acid

Intensity - 24

m/e	Relative Intensity		
	Experimental	Reference	Authentic
15	14	-	20
16	2	-	4
28	5	6	7
29	7	16	18
31	3	5	4
41	4	5	2
42	10	14	15

17. Acetic Acid -- (continued)

m/e	Relative Intensity		
	Experimental	Reference	Authentic
43	100	100	100
44	3	5	4
45	98	94	98
60	57	58	64

18. Methyl Formate

Intensity - 4

m/e	Relative Intensity		
	Experimental	Reference	Authentic
28	8	11	
29	73	78	
30	15	8	
31	100	100	
32	50	33	
60	38	32	

19. Furan

Intensity - 15

m/e	Relative Intensity		
	Experimental	Reference	Authentic
12	1	1	1
14	2	4	1
18	2	1	2
26	3	4	2
27	4	9	1
28	6	9	7
29	16	16	11
30	3	2	3
31	4	1	2
34	3	3	2
37	9	11	6
38	14	18	14
39	100	100	100
40	13	13	13
42	8	8	6
68	89	71	89
69	5	3	3

20. Cyclopentene

Intensity - 5

m/e	Relative Intensity		
	Experimental	Reference	Authentic
26	3	4	
27	18	15	
29	1	1	
39	40	38	
40	24	16	
41	21	19	
42	10	8	
53	29	23	
65	8	6	
66	9	10	
67	100	100	
68	55	43	

21. Methacrolein

Intensity - 10

m/e	Relative Intensity		
	Experimental	Reference	Authentic
15	4	4	
26	5	7	
27	12	16	
28	11	6	
29	15	16	
31	6	3	

21. Methacrolein -- (continued)

m/e	Relative Intensity		
	Experimental	Reference	Authentic
37	7	8	
38	12	11	
39	70	70	
41	100	100	
42	18	16	
43	11	24	
69	8	9	
70	71	70	

22. 2-Pentene

Intensity - 5

m/e	Relative Intensity		
	Experimental	Reference	Authentic
26	4	3	
27	21	21	
29	27	25	
31	4	2	
39	28	29	
40	7	5	
41	23	27	
42	44	43	
53	11	8	
54	6	3	
55	100	100	
70	37	35	

23. 2-Butenal

Intensity - 2

m/e	Relative Intensity		
	Experimental	Reference	Authentic
27	21	24	
28	30	34	
29	16	24	
38	16	21	
39	80	90	
40	14	5	
41	100	100	
42	10	4	
69	36	40	
70	80	83	

24. Pyruvaldehyde

Intensity - 12

m/e	Relative Intensity		
	Experimental	Reference	Authentic
14	9	14	
15	45	43	
29	28	28	
31	4	14	
42	10	10	
43	100	100	
45	15	21	
60	9	9	
72	3	2	

25. Benzene

Intensity - 4

m/e	Relative Intensity		
	Experimental	Reference	Authentic
37	3	2	3
38	5	4	5
39	16	11	15
50	16	14	16
51	20	17	20
52	24	18	22
77	18	15	17
78	100	100	100

26. 1,5-Hexadiene

Intensity - 70

m/e	Relative Intensity		
	Experimental	Reference	Authentic
15	3	4	
26	4	5	
27	23	29	
28	6	7	
29	7	6	
39	53	62	
40	7	7	
41	100	100	
42	6	6	
53	9	10	

26. 1,5-Hexadiene -- (continued)

m/e	Relative Intensity		
	Experimental	Reference	Authentic
54	51	54	
55	5	6	
67	72	83	
68	4	5	
81	6	7	
82	1	1	

27. 3-Methyl-1-pentene

Intensity - 2

m/e	Relative Intensity		
	Experimental	Reference	Authentic
27	45	48	
29	43	40	
39	41	36	
41	76	79	
55	100	100	
56	35	39	
69	66	71	
84	35	30	

28. 3-Hexene

Intensity - 2

m/e	Relative Intensity		
	Experimental	Reference	Authentic
27	32	38	
29	24	25	
39	35	38	
41	84	81	
42	73	69	
43	18	16	
53	13	10	
54	11	7	
55	100	100	
56	32	28	
69	39	30	
84	43	37	

29. 4-methyl-1,3-dioxolane

Intensity - 4

m/e	Relative Intensity		
	Experimental	Reference	Authentic
15	9	11	
27	14	16	
28	23	23	
29	41	46	
31	41	42	
39	10	5	

29. 4-methyl-1,3-dioxolane -- (continued)

m/e	Relative Intensity		
	Experimental	Reference	Authentic
41	18	16	
42	9	3	
43	26	22	
44	100	100	
45	20	22	
58	45	44	
87	54	51	
88	3	4	

Gas Chromatograph. The stream splitter was closed so that all of the column effluent was directed to the flame detector. Detector response factors were determined for all the components which appeared consistently in the product mixtures. These response factors were transformed in such a way that a value of unity was given to propylene. The response factors are listed in Table 3.

For compounds to which the flame detector did not respond, standard mixtures were prepared and analyses were performed utilizing the total ion monitor of the mass spectrometer as the detector.

Quantitative analyses were normally performed with 2 millliliter aliquots of the cell contents taken both before and after the irradiation period.

E. Reaction Studies

In all of the reaction studies, the cell, filled with the desired gas mixture, was positioned in the laser beam, irradiated for the desired length of time, and the reaction mixture was then analyzed. The procedures for obtaining the gas mixtures have been previously described. Proper alignment of the reaction cell in the laser beam path was accomplished either by using the Helium-Neon laser or by using the infrared laser adjusted to a low power. The power

TABLE 3

Response Factors for Flame Detector

Component	Response Factor
Methane	1.5 ± 0.2
Ethylene	0.51 ± 0.03
Ethane	0.50 ± 0.05
Propylene	1 ± 0.03
Propane	0.6 ± 0.1
Acetaldehyde	1.5 ± 0.1
1-Butene	0.82 ± 0.03
2-Butene	0.71 ± 0.03
Methanol	2.4 ± 0.5
2-Pentene	0.29 ± 0.05
Ethanol	1.9 ± 0.1
Propanal	1.1 ± 0.1
Acetone	1.0 ± 0.1
3-Hexene	0.30 ± 0.03
Acetic acid	3.1 ± 0.1
Hexadiene	0.43 ± 0.05
Benzene	0.32 ± 0.01

meter was placed in the laser beam path, between the laser and the cell, in order to adjust the laser output power to the desired level. Irradiation of the gas mixture was begun by moving the power meter out of the laser beam path. After the desired irradiation time, the laser was turned off and the cell was removed for analysis of the contents.

1. Initial Studies With the Large Cells

a. Studies Performed in the 54 Centimeter Cell

After the initial observation of the formation of a small amount of condensate inside the cell during a fluorescence experiment, the large cell shown in Figure 1 was constructed for study of this reaction. The cell was somewhat larger than the one used in the fluorescence experiment. The size was intended to eliminate heating effects as much as possible. All of the studies utilizing the large cells were done with the laser output power at 35 watts.

Several different concentrations of oxygen in propylene, sealed in the cell, were irradiated for periods of time up to one hour. Gas chromatographic analysis of the gaseous mixtures, after irradiation, showed no detectable products. No condensate was noted in the reaction cell.

The apparent amount of reaction products in the fluorescence experiment was small. It was believed that

larger quantities of products might be obtained by flowing the propylene-oxygen mixture through the cell during irradiation and by utilizing a cold trap (ice) to condense the reaction products after their exit from the cell. After several trials, it was found that a mixture of 80% propylene and 20% oxygen, flowing at rates of 48 and 12 cubic centimeters per minute respectively, gave the best results. After irradiation periods of up to 1 hour, however, only a very small amount of condensate was found in the cold trap and nothing was found in the cell itself. The substance was found to be soluble in carbon tetrachloride. Analysis of the carbon tetrachloride solution was attempted using the gas chromatograph-mass spectrometer combination. There was not enough product present, however, to obtain useful spectra.

Studies Performed in the 22 Centimeter Cell

It was reasoned that the cell was too large. The calculated volume of the laser beam was only about 2% of the total cell volume. However, the laser beam was completely absorbed by the gas in the cell and probably only the first several centimeters of the cell length were involved. The smaller, 22 centimeter cell was built then and put into use. The calculated laser beam volume here was 4% of the total

cell volume.

The optimum experimental conditions previously described were utilized with the new cell. After irradiation for 20 minutes, a small amount of a white, waxy appearing material formed in the cold trap. Continued irradiation of the flowing system resulted in a very slow increase in the amount of material in the cold trap. This increase in the amount of material stopped after about an hour of irradiation. The flow was then stopped, the cell sealed, and the system irradiated for an additional 15 minutes to see if anything could be formed inside the cell itself. A small amount of white appearing material was also seen to form on the insides of the cell walls. Continued irradiation resulted in no visible change in the amount of condensate.

Analysis of the gaseous cell contents using the gas chromatograph-mass spectrometer combination showed only propylene and essentially trace amounts of ethylene, ethane, and an unidentifiable substance in the C_4 range of molecular weights. Both the cold trap material and the condensate from the cell were dissolved in carbon tetrachloride. The carbon tetrachloride was allowed to evaporate and a yellow, viscous liquid remained. Infrared analysis of the material indicated that it was composed of saturated, long-chain

hydrocarbons (Figure 8). Sixty, one hundred, and three hundred Megahertz NMR spectra obtained from the material also indicated a mixture of saturated hydrocarbons with some branching along the chain (Figures 9, 10, and 11). Integration gave an average methylene proton to methyl proton ratio of 3 to 1. A similarly integrated spectrum of polypropylene should give a 1 to 1 ratio. This indicated that the compounds were not simply different lengths of ordinary polypropylene. The reaction was not, then, a simple free radical polymerization of propylene.

Utilizing the OV-1 column for separation, the mixture was analyzed by the gas chromatograph-mass spectrometer technique. The substance was found to be a mixture of long-chain hydrocarbons ranging from C_{20} to greater than C_{28} compounds. The gas chromatograph recorder trace is shown in Figure 12. The quantity of products was small and the mixture was complex, consequently, no separation into individual components for analysis was possible and no quantitative analysis was attempted.

The fact that the formation of the products in the cold trap and in the cell appeared to stop after a time suggested that perhaps there was some sort of surface phenomenon involved. To investigate the effect of increased surface area on product yield, the 22 centimeter cell was

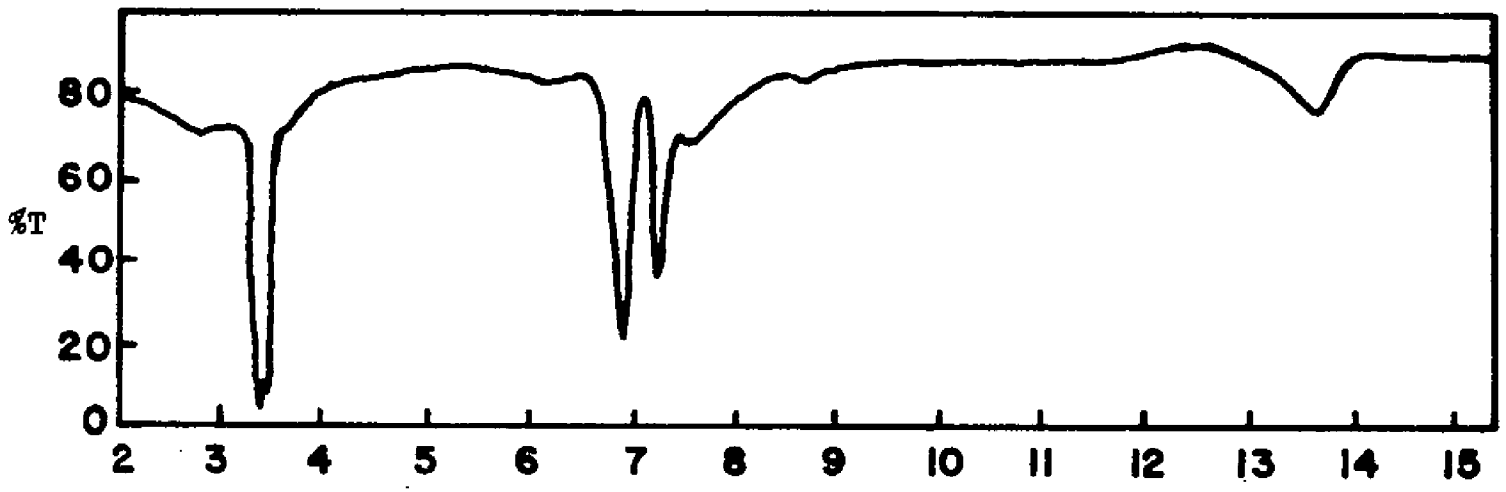


Figure 8. INFRARED ABSORPTION SPECTRUM OF LIQUID REACTION PRODUCT MIXTURE

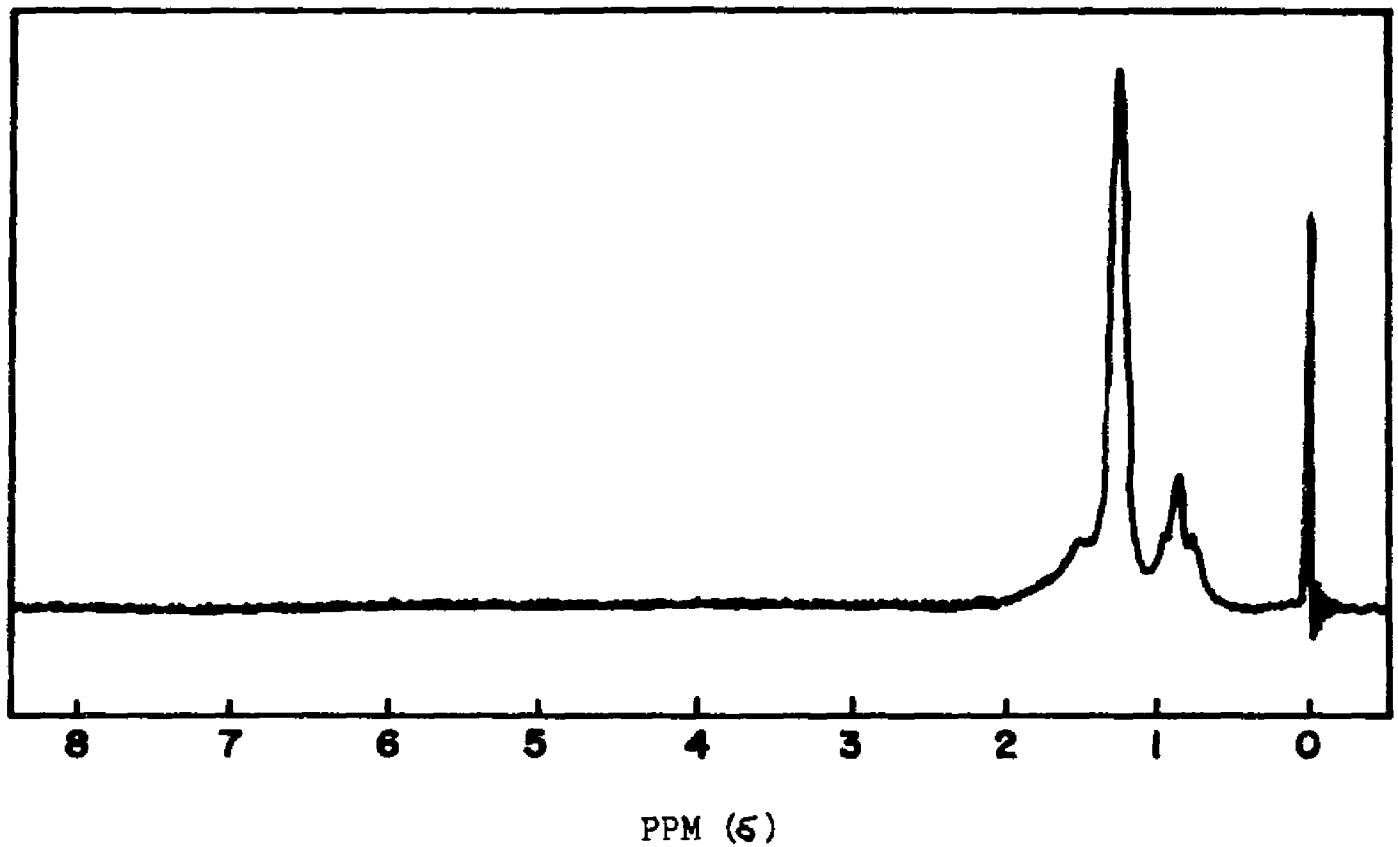


Figure 9. 60 MHz NMR SPECTRUM OF LIQUID REACTION PRODUCT MIXTURE

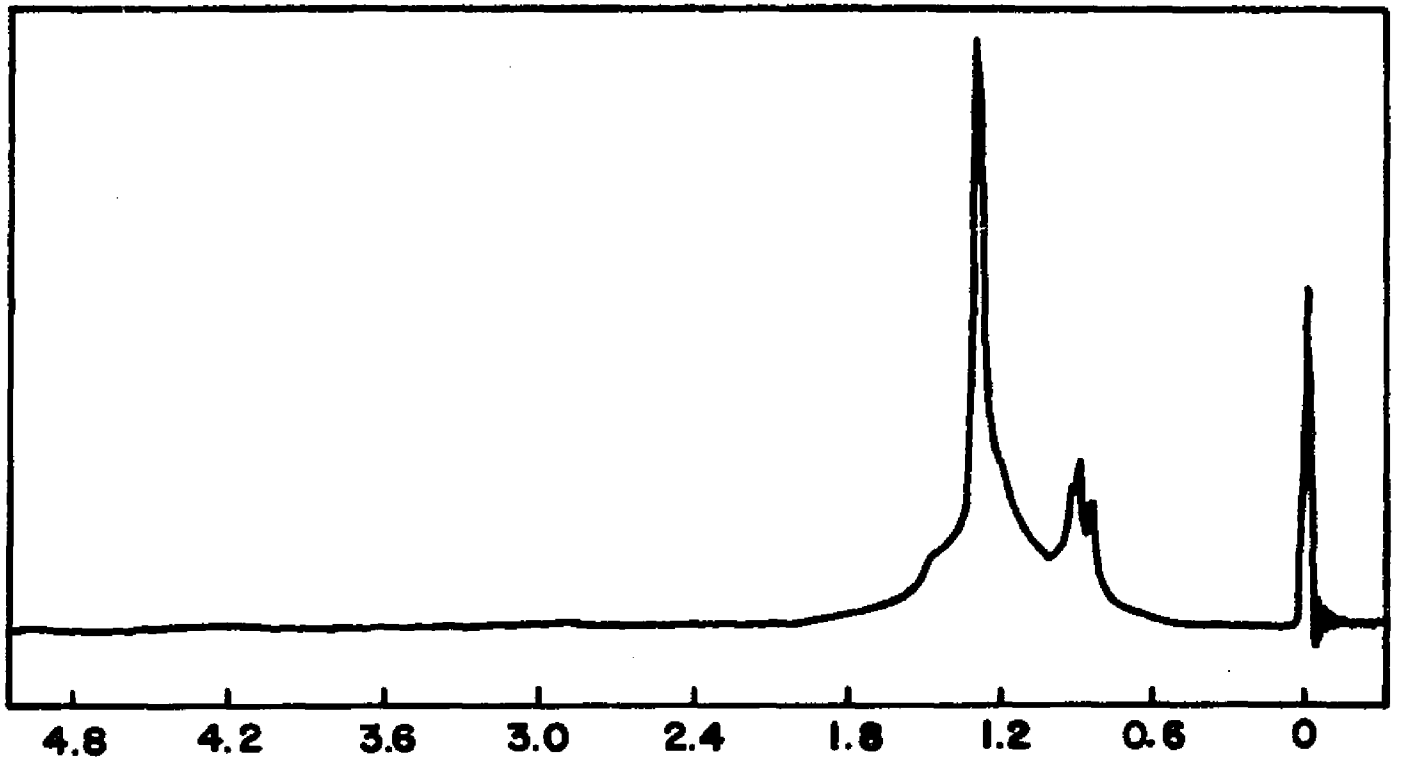


Figure 10. 100 MHz NMR SPECTRUM OF LIQUID REACTION PRODUCT MIXTURE

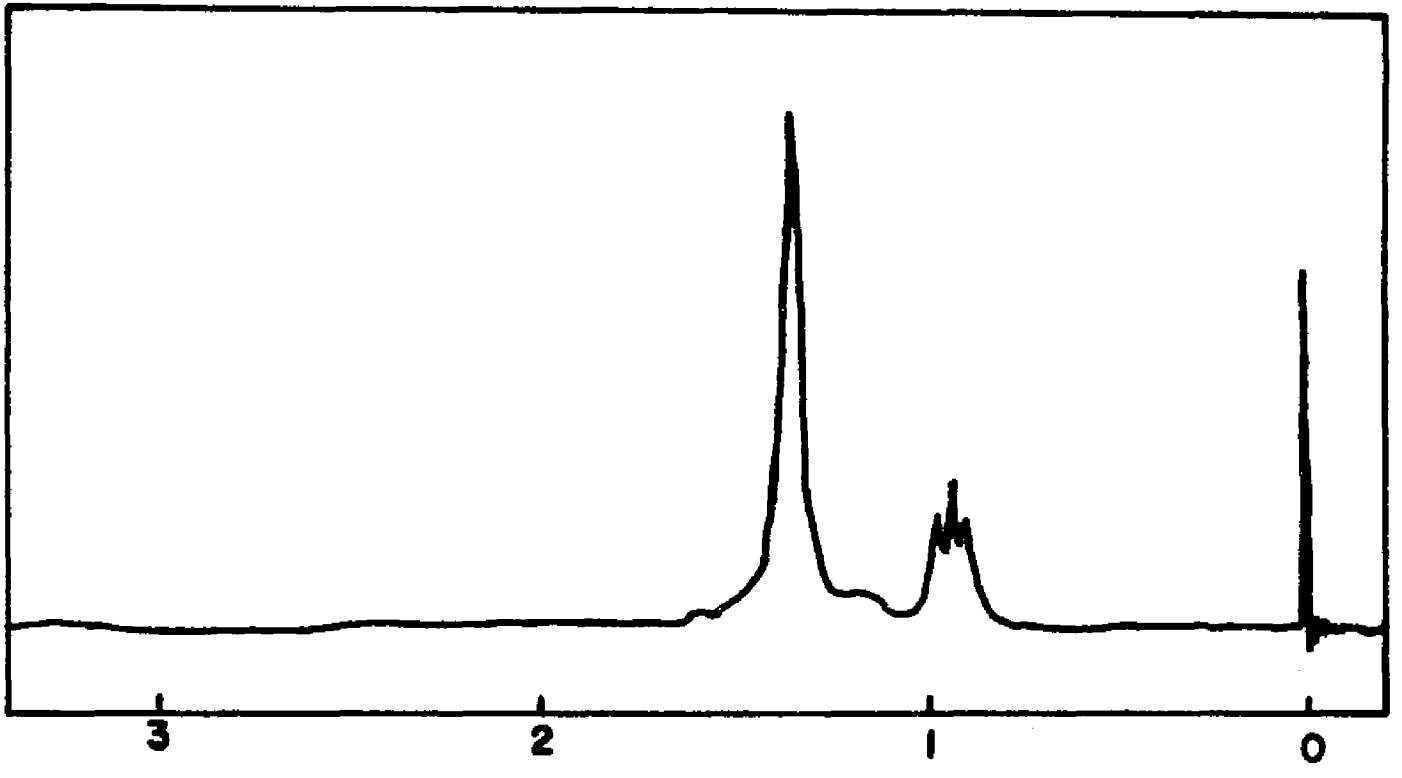


Figure 11. 300 MHz NMR SPECTRUM OF LIQUID REACTION PRODUCT MIXTURE

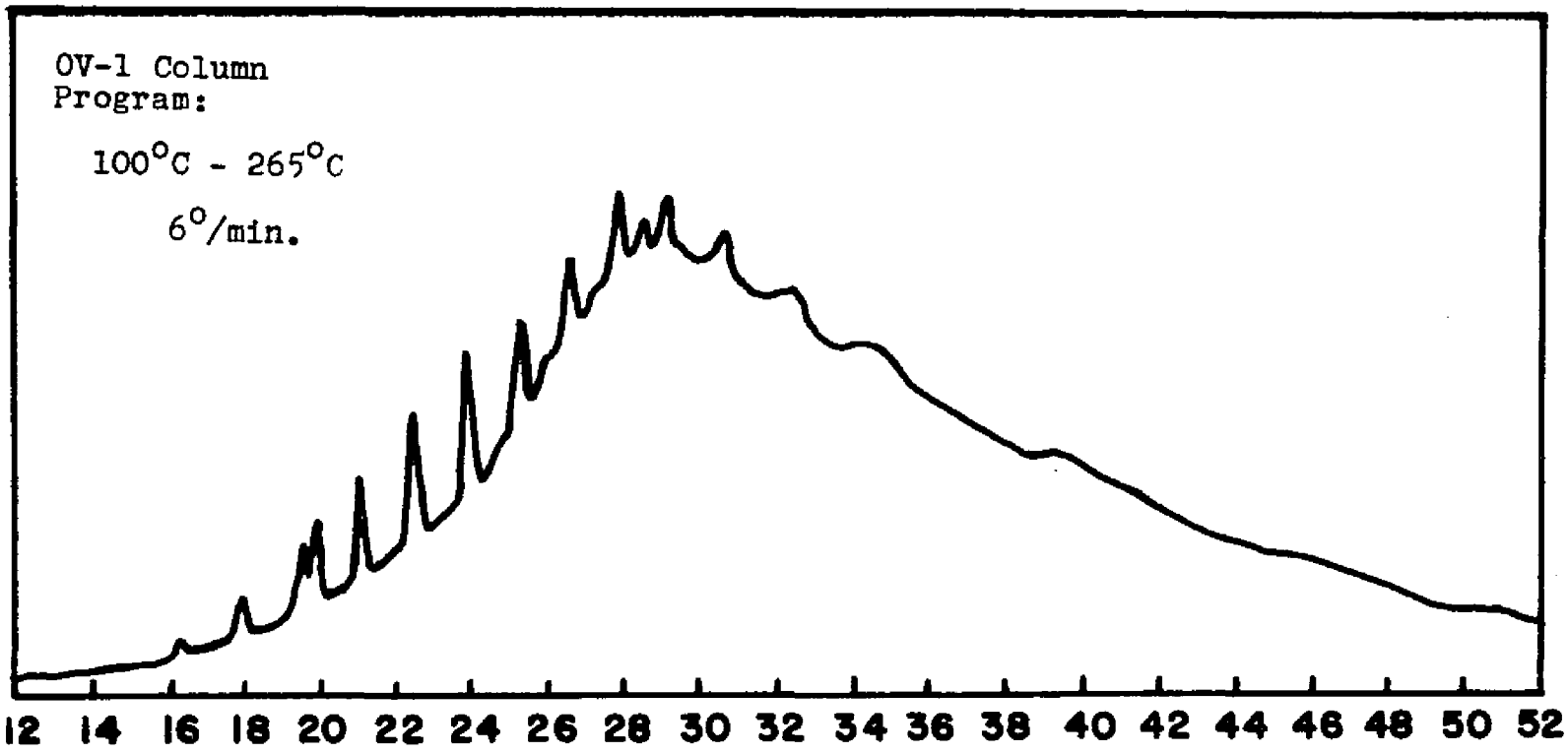


Figure 12. GAS CHROMATOGRAPH OF LIQUID HYDROCARBON MIXTURE

packed with glass wool with a hole being left down the center to allow passage of the laser beam. Repeating the experiment as before gave little, if any, improvement with respect to product yield.

The mere formation of this material was very unique and unexpected under the specified conditions. The fact that the structures of the compounds did not appear to be the same as polypropylene was further puzzling.

2. Reaction Studies In Small Cells

In order to see if a smaller cell would enhance the reaction, the 18 centimeter cell shown in Figure 1 was built and put into use. With the use of this cell, the character of the reaction seemed to change. Several different concentrations of oxygen in propylene yielded gaseous products in measurable quantities after only a short period of irradiation. Furthermore, irradiation with the laser output power at 20 watts also caused a reaction to take place between the propylene and oxygen. The 20 watt irradiations, however, caused different extents of reaction and different product distributions than those obtained with 35 watts. The high molecular weight alkanes were not detected at all as products from these reactions in the small cells. All of the reactions in the small cells were carried

out with sealed, non-flowing systems.

a. Studies at a Laser Beam Power of 20 Watts

All irradiations were carried out for 30 minutes and the amounts of products are reported as percentages of total identified products.

i. 100% Propylene

Irradiation of 100% propylene yielded no detectable products as measured by the Perkin-Elmer 990 Gas Chromatograph. Propylene alone, then, does not undergo a detectable reaction under the influence of the 20 watt laser irradiation. The absorption of laser energy was apparently insufficient to cause bond breakage, either directly or as a result of the collisions of excited propylene molecules.

ii. Reaction of 90% Propylene - 10% Oxygen

Irradiation of a mixture of 90% propylene and 10% oxygen resulted in a 0.1% conversion of propylene to products. The product distribution is shown in Table 4. The addition of the oxygen resulted in a reaction even at this relatively low laser power. The extent of reaction was, however, very small and it was noted that practically all of the product was acetaldehyde. The propylene obviously interacted with the oxygen to form acetaldehyde as the initial product.

TABLE 4

Products From Irradiation of a 90:10 Propylene-Oxygen Mixture Utilizing Low Laser Beam Power

Product	Percent of Products
Methane	0.5
Ethylene	0.4
Ethane	0.5
Acetaldehyde	98.6
Conversion of propylene	0.1%

iii. Reaction of 70% Propylene - 30% Oxygen

Irradiation of a mixture of 70% propylene and 30% oxygen resulted in 4% conversion of the propylene to products. The product distribution is shown in Table 5. The increased amount of oxygen caused an increase in the extent of reaction as well as a different product distribution from that of the 90% - 10% mixture. The reaction is seen to be dependent upon the oxygen concentration at a laser beam power of 20 watts.

b. Studies at a Laser Beam Power of 35 Watts

In all of the studies performed at 35 watts, the irradiation time was 30 minutes. The amounts of products are reported as percentages of total identified products.

i. 100% propylene

Numerous irradiations of what was presumably 100% propylene yielded oxygenated reaction products along with other compounds. This indicated that there was either an oxygen impurity in the propylene or that perhaps the epoxy cement, which held the Irtran-2 windows in place, released oxygen into the cell when heated by the laser beam. To eliminate the epoxy cement as a possible source of oxygen, the cell shown in Figure 2 was constructed and used. Irradiation of 100% propylene in this cell, however, still gave

TABLE 5

Products From Irradiation of a 70:30 Propylene-Oxygen Mixture Utilizing Low Laser Beam Power

Product	Percent of Products
Methane	0.5
Ethylene	0.3
Ethane	0.2
Acetaldehyde	65.3
Propanal	16.4
Acetone	17.3
Conversion of propylene	4%

oxygenated products. The propylene was passed over copper turnings heated to 200°C to remove oxygen, and then over Drierite to remove water. This "scrubbed" propylene was then injected into an evacuated cell. After this was done, laser irradiation resulted in no detectable reaction.

This was a very significant result in that it showed that oxygen was necessary for the reaction, even at a laser power of 35 watts. The reaction was apparently the result of the interaction of an excited species of propylene with oxygen. Direct interaction of the laser beam with the propylene did not result in any bond scission. Breakage of the pi bond in propylene by direct absorption of 10.6 micron laser energy would require the absorption of 25 photons of energy per propylene molecule.

ii. Reaction of 90% Propylene - 10% Oxygen

Irradiation of a mixture of 90% propylene and 10% oxygen resulted in 16% conversion of the propylene to products. The product distribution is shown in Table 6. As previously noted, the same concentrations of gases gave only 0.1% conversion when exposed to laser radiation at 20 watts. Increasing the laser power to 35 watts caused a marked increase in the extent of reaction. It is seen from the table that the increased extent of reaction was accom-

TABLE 6

Products From Irradiation of a 90:10 Propylene-Oxygen Mixture Utilizing High Laser Beam Power

Product	Percent of Products
Methane	10.0
Carbon dioxide	0.6
Ethylene	15.4
Ethane	0.7
Water	0.1
Acetaldehyde	33.4
1-Butene	11.2
trans-2-Butene	4.6
cis-2-Butene	3.0
Propylene oxide	3.2
Propanal	5.8
Acetone	4.9
Hexadiene	5.7
4-methyl-1,3-Dioxolane	1.4
Conversion of propylene	16%

panied by the appearance of a number of previously undetected products and a decrease in the relative amount of acetaldehyde.

iii. Reaction of 70% Propylene - 30% Oxygen

Irradiation of a 70% propylene and 30% oxygen mixture resulted in the formation of a liquid condensate inside the cell after about 1 minute of exposure to the laser beam. This material increased in quantity until it coated the inside of most of the cell at the end of 30 minutes. Analysis indicated a 27% conversion of the propylene to products and the gas phase products were essentially the same as those obtained from the 90% propylene and 10% oxygen reaction. The distribution of the gaseous products is shown in Table 7.

The liquid contents of the cell were removed and analyzed. Fifteen components were identified in the mixture, some of which were the same as those detected in the gas phase and some of which were not. The products identified are listed in Table 8. No attempt was made at quantitative analysis because many of the components were quite volatile and varying amounts were certainly lost by evaporation during the process of recovery from the cell.

Acetaldehyde was always seen as a major product

TABLE 7

Products From Irradiation of a 70:30 Propylene-Oxygen Mixture Utilizing High Laser Beam Power

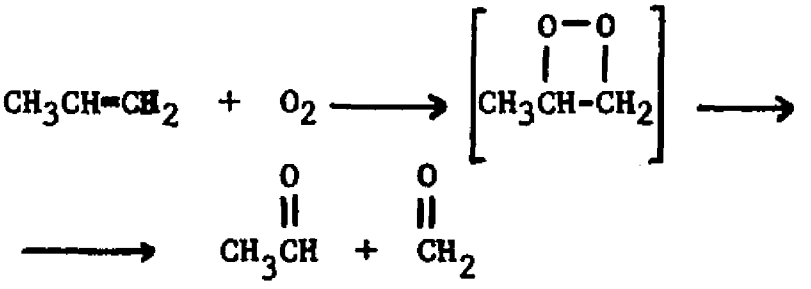
Product	Percent of Products
Methane	7.6
Carbon dioxide	4.9
Ethylene	9.1
Ethane	0.6
Water	1.9
Acetaldehyde	30.7
1-Butene	8.9
trans-2-Butene	5.9
cis-2-Butene	2.4
Propylene oxide	11.8
Propanal	5.4
Acetone	3.6
Hexadiene	5.8
4-methyl-1,3-Dioxolane	1.4
Conversion of propylene	27%

TABLE 8

Liquid Products From Irradiation of a 70:30 Propylene-Oxygen Mixture Utilizing High Laser Beam Power

Product
Methane
Carbon dioxide
Formaldehyde
Water
Acetaldehyde
Methyl formate
Ethanol
Furan
Acetone
Allyl alcohol
Methacrolein
Hexadiene
4-methyl-1,3-Dioxolane
Benzene
Pyruvaldehyde

in the small cell studies. A plausible mechanism for the formation of acetaldehyde involves the combination of an excited propylene molecule with oxygen to form a 1,2-dioxetane as an intermediate. The unstable dioxetane cleaves to give acetaldehyde and formaldehyde.



It therefore seemed reasonable to expect formaldehyde to also appear as a major product. Formaldehyde, however, was never detected in any of the gas phase products . The appearance of the formaldehyde in the liquid products of this reaction was very revealing. The retention time of formaldehyde was found to be such that it would always elute with the propylene in the gas phase analysis. There was always so much unreacted propylene in the cell that its peak on the gas chromatographic recorder trace would completely cover up any formaldehyde peak that might be present. The presence of the formaldehyde in the liquid phase indicated that it was formed in the reaction and was quite probably present in the other gaseous products.

c. Thermal Studies

Absorption of the laser radiation by the Irtran windows and by the propylene in the cell always caused an increase in the thermal energy of the propylene, as evidenced by a warming of the glass cell. It was questioned whether the observed reactions were caused by increased thermal energy.

The reaction cell shown in Figure 3 was constructed and used in order to get a measurement of the temperature inside the cell during an experiment. The cell was constructed in such a way that the bulb of the thermometer was a calculated 5 millimeters from the outer edge of the laser beam. All of the experiments conducted with the laser output power at 35 watts were repeated with this cell. The highest temperature observed was 57^{o}C. This temperature was observed with the 100% propylene experiment.

The 18 centimeter cell was filled with 90% propylene and 10% oxygen and heated thermally to 200^{o}C to compensate for any discrepancy between the measured temperature in the cell and the temperature in the beam. The temperature was kept at 200^{o}C for 1 hour. Gas chromatographic analysis indicated that no reaction had taken place. The reactions, then, were apparently not primarily thermal in nature.

3. Acetaldehyde Reaction Studies

It was noted that in the studies of propylene - oxygen systems performed at a laser power of 20 watts, acetaldehyde constituted practically all of the reaction product mixture. In the similar studies performed at 35 watts, the acetaldehyde was still detected as a major product, but its percentage in the reaction mixture had been dramatically reduced. This suggested that acetaldehyde was formed as an initial product of the reaction between propylene and oxygen and that, at high laser power, it then reacted to form other products. Acetaldehyde was found to absorb infrared radiation at 10.6 microns rather strongly (Figure 13) thus providing a basis for interaction with the laser beam and giving further support to the idea suggested above.

Studies were conducted on several acetaldehyde systems to test the hypothesis. All of these reactions were carried out in the 18 centimeter cell illustrated in Figure 1. Gases and gas mixtures for reaction studies were obtained by injection of the desired amounts into an evacuated cell. All of the acetaldehyde studies were performed at a laser power of 35 watts and with irradiation periods of 15 minutes.

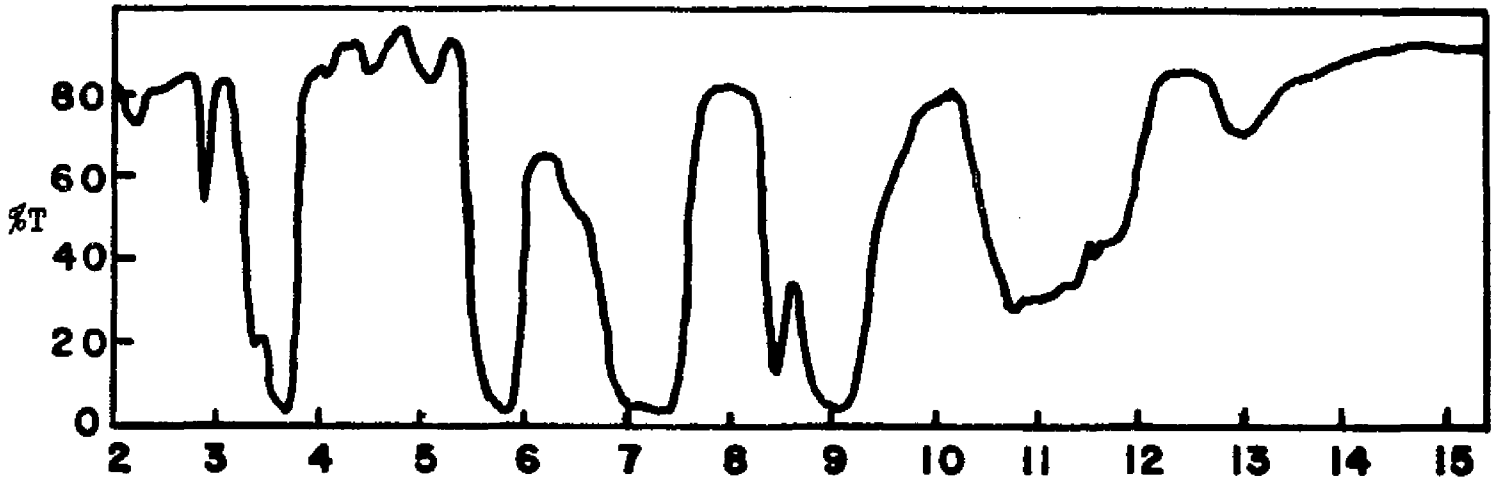


Figure 13. INFRARED ABSORPTION SPECTRUM OF ACETALDEHYDE

a. Reaction of 100% Acetaldehyde

Irradiation of 100% acetaldehyde caused a reaction to take place, with 16% of the acetaldehyde being converted to products. Analysis of the gaseous mixture gave the product distribution shown in Table 9. Carbon monoxide was detected by the mass spectrometer but no quantitative information was obtained on it because the retention time of carbon monoxide was so similar to that of methane that resolution was impossible.

These products and their distributions are in good agreement with those reported by Laidler and Liu[37] for the thermal decomposition of acetaldehyde at 523°C. It should be pointed out again, however, that the highest temperature observed in a reaction cell in these studies was 57°C. To explain their results, Laidler and Liu proposed the following mechanism, the first five reactions of which are the original Rice and Herzfeld scheme[38].

(1) $CH_3CHO \longrightarrow {}^{\cdot}CH_3 + {}^{\cdot}CHO$

(2) ${}^{\cdot}CHO \longrightarrow CO + {}^{\cdot}H$

(3) ${}^{\cdot}H + CH_3CHO \longrightarrow H_2 + CH_3\dot{C}O$

(4) ${}^{\cdot}CH_3 + CH_3CHO \longrightarrow CH_4 + CH_3\dot{C}O$

(5) $CH_3\dot{C}O \longrightarrow {}^{\cdot}CH_3 + CO$

(6) ${}^{\cdot}CH_3 + CH_3CHO \longrightarrow {}^{\cdot}CH_2CHO + CH_4$

(7) ${}^{\cdot}CH_2CHO \longrightarrow CH_2CO + {}^{\cdot}H$

TABLE 9

Products From Irradiation of 100% Acetaldehyde

Product	Percent of Products
Methane	99.0
Ethane	0.8
Propanal	0.1
Acetone	0.1

Conversion of acetaldehyde 16%

Conditions: Laser beam power at 35 watts.
15 minute period of irradiation

$$(8)\quad \cdot CH_3 + CH_3CHO \longrightarrow CH_3COCH_3 + \cdot H$$

$$(9)\quad \cdot CH_3 + \cdot CH_3 \longrightarrow C_2H_6$$

$$(10)\quad \cdot CH_3 + \cdot CH_2CHO \longrightarrow CH_3CH_2CHO$$

It should be pointed out that the CH_2CO (ketene), although stable under the reaction conditions, was not detected as a final reaction product.

The presence of these radicals in the propylene reaction would adequately explain most of the observed products.

b. Reaction of 90% Acetaldehyde and 10% Oxygen

Irradiation of a mixture of 90% acetaldehyde and 10% oxygen resulted in 39% conversion of the acetaldehyde to products. Ten products were present in quantities large enough for identification. These products and their distributions are shown in Table 10. Once again methane made up most of the product mixture and carbon monoxide was detected only by the mass spectrometer.

Acetic acid, which was formed in this reaction, was found to absorb infrared radiation at 10.6 microns (Figure 14) thus giving a basis for its interaction with the laser beam. Bamford and Dewar[39] decomposed acetic acid at 500°C and reported the following reactions:

TABLE 10

Products From Irradiation of a 90:10 Acetaldehyde-Oxygen Mixture

Product	Percent of Products
Methane	86.8
Ethylene	0.4
Ethane	5.1
Propylene	0.1
Propane	0.3
Methanol	1.8
Propanal	0.9
Acetone	0.6
Acetic Acid	4.0

Conversion of acetaldehyde 16%

Conditions: Laser beam at 35 watts.
15 minute irradiation period.

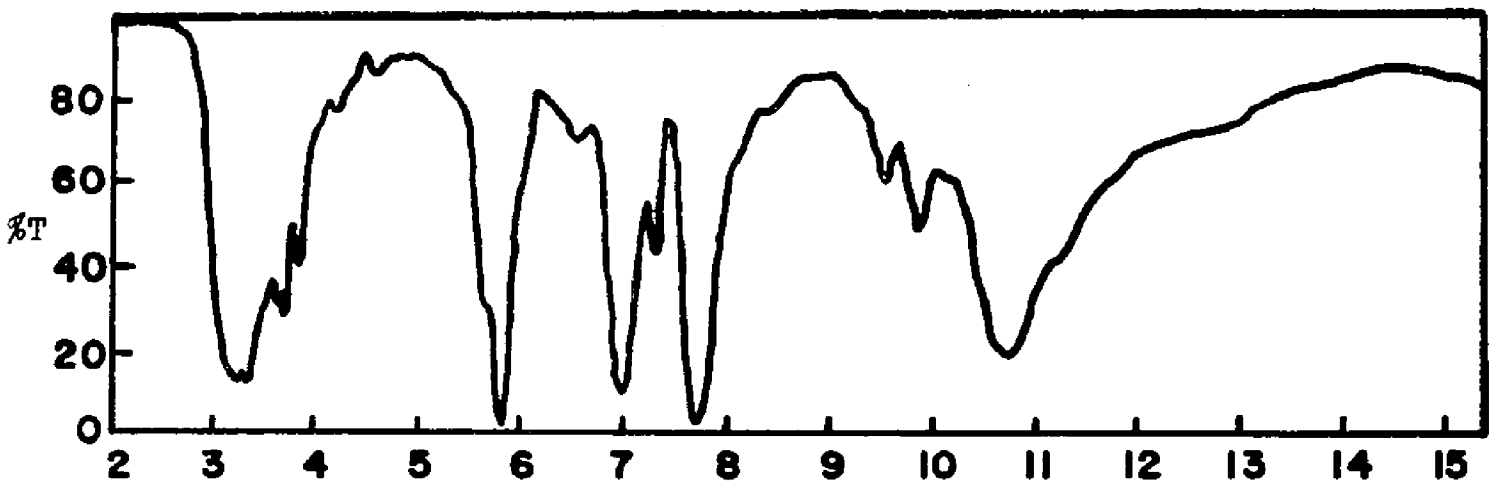


Figure 14. INFRARED ABSORPTION SPECTRUM OF ACETIC ACID

(1) $CH_3COOH \longrightarrow CH_2{=}C{=}O + H_2O$

(2) $CH_3COOH \longrightarrow CH_4 + CO_2$

(3) $2CH_2{=}C{=}O \longrightarrow CH_4 + C + 2CO$

(4) $2CH_2{=}C{=}O \longrightarrow C_2H_4 + 2CO$

Ketene is again seen as a product. Ketene also absorbs infrared radiation at 10.6 microns (Figure 15) and is known to decompose both thermally and photolytically to form methylene[40]. The presence of methylene in the propylene - oxygen reaction would readily explain the formation of many of the reaction products.

c. Acetaldehyde - Propylene - Oxygen Systems

The effect of added acetaldehyde on the propylene-oxygen reaction was investigated. A mixture of 90% propylene and 10% acetaldehyde was first studied to see the effect of acetaldehyde in the absence of oxygen. This was followed by a study of a mixture of 89% propylene - 10% acetaldehyde - 1% oxygen.

i. Reaction of 90% Propylene-10% Acetaldehyde

Propylene was made oxygen-free by passing it over heated copper turnings in order to avoid a possible laser induced reaction with oxygen. Exposure of a mixture of 90% oxygen-free propylene and 10% acetaldehyde to the laser

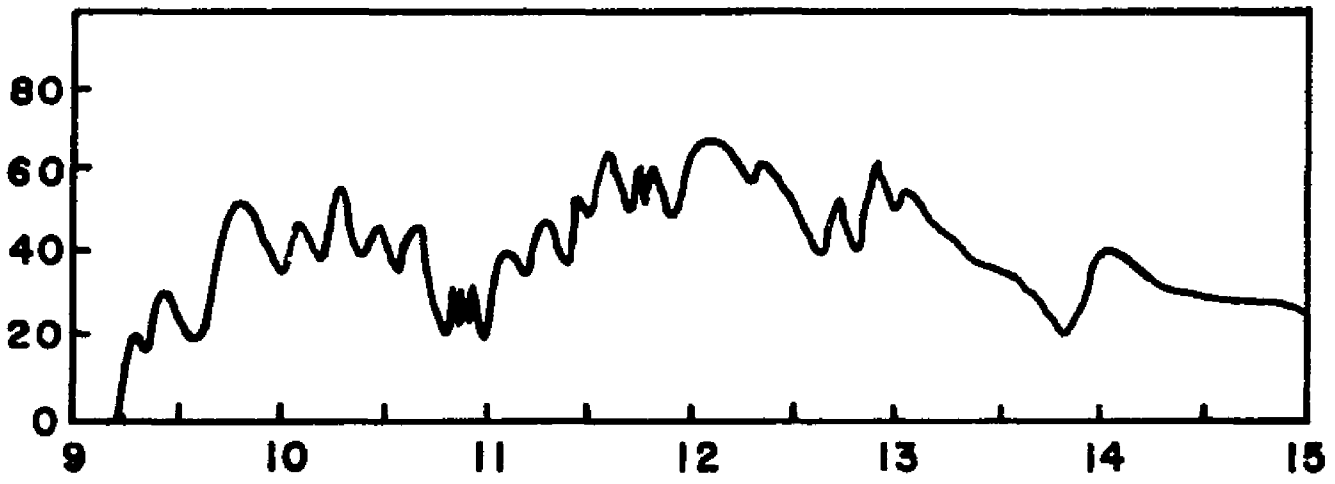


Figure 15. INFRARED ABSORPTION SPECTRUM OF KETENE

radiation induced a reaction in which 3% of the propylene and 22% of the acetaldehyde were converted to products. Table 11 lists the products and their relative percentages. Carbon monoxide was detected by the mass spectrometer, but as pointed out before, poor resolution from methane made quantitative analysis impossible.

This reaction, in the absence of molecular oxygen, showed convincingly that the acetaldehyde did indeed react to give intermediate species which then reacted with propylene. The products and their distributions in this reaction were considerably different from those of the 100% acetaldehyde reactions. Also, as was shown previously, 100% propylene gave no reaction.

ii. Reaction of 89% Propylene - 10% Acetaldehyde - 1% Oxygen

Reaction of a mixture of 89% propylene, 10% acetaldehyde, and 1% oxygen under the influence of the laser beam resulted in a conversion of 2% of the propylene and 21% of the acetaldehyde to products. This was essentially the same conversion as with the 90% propylene and 10% acetaldehyde but the products were different, as were the distributions. The products are listed in Table 12. Again, carbon monoxide was detected only by the mass spectrometer.

TABLE 11

Products From Irradiation of a 90:10
Propylene-Acetaldehyde Mixture

Products	Percent of Products
Methane	6.4
Ethylene	2.2
Ethane	2.1
1-Butene	52.9
Hexadiene	36.4

Conversion of propylene	3%
Conversion of acetaldehyde	22%

Conditions: Laser beam power at 35 watts.
15 minute irradiation period.

TABLE 12

Products From Irradiation of an 89:10:1
Propylene-Acetaldehyde-Oxygen Mixture

Products	Percent of Products
Methane	9.6
Ethylene	8.2
Ethane	1.8
1-Butene	26.1
trans-2-Butene	13.0
cis-2-Butene	5.8
Propylene oxide	5.1
Propanal	8.8
Acetone	10.0
Hexadiene	11.6
Conversion of propylene	2%
Conversion of acetaldehyde	21%

Conditions: Laser beam power at 35 watts.
15 minute period of irradiation.

The products formed in this reaction were essentially the same as those formed in the 35 watt irradiations of the propylene - oxygen mixtures. The distributions, however, were different.

4. Detection of Methylene Species

The presence of ethylene, 2-butene, and 4-methyl-1,3-dioxolane in the propylene - oxygen reaction products suggested the possible existence of methylene in the reaction mixture. The detection of acetic acid as a product in reactions involving acetaldehyde and oxygen, and the reported decomposition of acetic acid to ketene, also raised the question of the existence of methylene as an intermediate in the propylene - oxygen reaction.

Methylene exists in two electronically different states, the singlet and triplet, of which the triplet is the more stable. A characteristic reaction of singlet methylene is insertion into C-H bonds and cycloaddition to double bonds.[41] An investigation into the possible formation of singlet methylene was conducted with propane as the trapping agent. Propane does not absorb infrared radiation at the wavelength of the laser beam. Insertion into the C-H bonds of propane should produce butane and isobutane in a 3:1 ratio since singlet methylene is reported to be rela-

tively unselective.[42]

1,3-butadiene was used as the trapping species in an investigation of the possible formation of triplet methylene. 1,3-butadiene is capable of reacting with triplet methylene in a two step addition process to give cyclic products. The addition is reported to proceed in a 1,2 or 1,4 manner, giving vinyl cyclopropane and cyclopentene.[43] The appearance of either as a reaction product would be evidence for triplet methylene.

a. Propane Study

A mixture of 90% propane, 5% acetaldehyde, and 5% oxygen was irradiated for 15 minutes. Analysis of the product mixture showed no butane or isobutane. It appears that singlet methylene was not formed during the reaction, or if it was formed, it was in insufficient quantity to give detectable insertion products. Supportive evidence for singlet methylene not having been formed in the reactions is in the fact that methylcyclopropane (which would form by cycloaddition of singlet methylene to propylene) was never detected as a reaction product.

b. 1,3-Butadiene Study

1. Reaction of 80% 1,3-Butadiene and 20% Oxygen

1,3-Butadiene absorbs 10.6 micron infrared radiation and reacts with oxygen when a mixture of the two gases is exposed to the laser beam. Consequently, when analyzing the reaction products from a butadiene - acetaldehyde - oxygen mixture, it was necessary to differentiate between those products formed from the mixture containing acetaldehyde. In order to do this, a mixture of 80% 1,3-butadiene and 20% oxygen was subjected to laser radiation for 15 minutes. Analysis of the gas phase products gave the product distribution shown in Table 13 with a 2% conversion of the 1,3-butadiene to products. Neither cyclopentene nor vinyl cyclopropane was detected as a product of this reaction.

ii. Reaction of 1,3-Butadiene - Acetaldehyde - Oxygen

A mixture of 35% 1,3-butadiene, 55% acetaldehyde, and 10% oxygen was irradiated for 15 minutes and the products analyzed. 25% of the acetaldehyde and 34% of the 1,3-butadiene were converted to products, the distribution of which is shown in Table 14. Vinyl cyclopropane was not detected but cyclopentene constituted 2% of the reaction products. This was taken as confirmatory evidence for the formation of triplet methylene in the reaction mixture.

TABLE 13

Products From Irradiation of an 80:20
1,3-Butadiene-Oxygen Mixture

Products	Percent of Products
Ethylene	2.9
Propylene	63.8
Acetaldehyde	8.7
Furan	2.9
Acrolein	11.6
2-Butenal	10.1
Conversion of 1,3-Butadiene	2%

Conditions: Laser beam power of 35 watts.
15 minute irradiation period.

TABLE 14

Products From Irradiation of a 35:55:10

1,3-Butadiene-Acetaldehyde-Oxygen Mixture

Products	Percent of Products
Methane	9.0
Ethylene	2.0
Ethane	0.2
Propylene	43.6
Furan	1.9
Acrolein	7.7
2-Pentene	2.1
Cyclopentene	2.0
3-methyl-1-Butene	0.8
3-Hexene	1.2
2-Butenal	7.4
A C_7H_{10}	6.1
Conversion of 1,3-butadiene	34%
Conversion of acetaldehyde	25%

Conditions: Laser beam power at 35 watts.
15 minute period of irradiation.

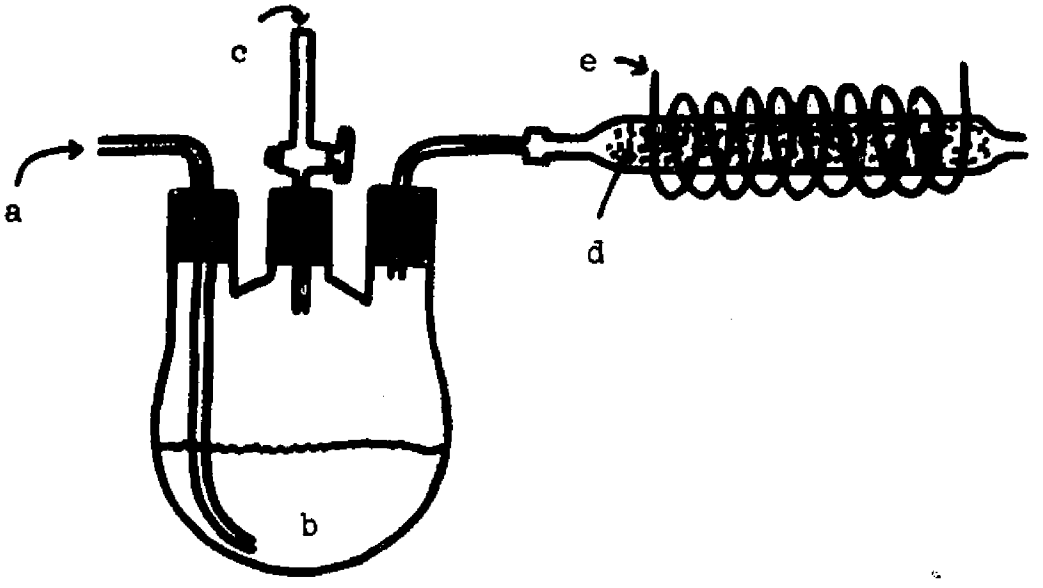
PART II

A. Studies on the Trapping Efficiencies of Various Trapping Agents for Sulfuric Acid Aerosol

The trapping efficiencies of fluoropore filter material (0.5 micron pore size), water, sodium carbonate solution, and sodium hydroxide solution for freshly generated sulfuric acid were investigated. This was by no means intended to be an exhaustive study of all of the trapping agents in use. It was intended to be primarily a study of two of the most widely used traps - fluoropore filters and water. The alkaline traps were intended to trap any radioactive sulfuric acid that may have passed through the preceeding traps to prevent escape into the air and, hopefully, to show the difficulty in trapping freshly generated sulfuric acid - even in alkaline solutions.

1. Generation of Sulfuric Acid

Sulfur dioxide was generated by the reaction of hydrochloric acid with sodium sulfite in aqueous solution. Sulfuric acid was generated from the sulfur dioxide by passing the sulfur dioxide, along with air and water vapor, over platinum catalyst heated to 400°C. The experimental arrangement is shown in Figure 16.



a. Air

b. $Na_2SO_3 + Na_2{}^{35}SO_3$

c. HCl

d. Platinum

e. Heater

Figure 16. EXPERIMENTAL ARRANGEMENT FOR GENERATION OF SULFURIC ACID AEROSOL

Sulfur dioxide is quite soluble in water so that relatively large quantities had to be generated in order for a suitable amount to bubble out of solution. A trial and error procedure was followed until suitable concentrations and amounts of hydrochloric acid and sodium sulfite were determined. The West-Gaeke test[44] was employed to determine the amount of sulfur dioxide generated in these initial studies.

Twenty four milliliters of solution containing 0.013 grams of sodium sulfire per milliliter were placed in a 3-necked fifty milliliter flask along with one milliliter of labelled sodium sulfite solution. The concentration of the labelled sodium sulfite was 2×10^{-7} grams per milliliter, so that its contribution to the sodium sulfite in solution was negligible but it gave the 25 milliliters of solution an activity of approximately 4,000 disintegrations per minute per milliliter. Air was bubbled through the solution at a rate of 100 cubic centimeters per minute. One milliliter of a hydrochloric acid solution containing 0.19 grams of hydrochloric acid per milliliter was then added to the sodium sulfite solution through a buret over a period of 10 minutes. The air, saturated with water vapor, carried a portion of the sulfur dioxide thus generated over the platinum catalyst heated to 400°C, where the conversion of

sulfur dioxide to sulfur trioxide and thence to sulfuric acid was accomplished.

The amount of sulfur dioxide evolved in this fashion varied slightly from one experiment to the next (as indicated by the West-Gaeke test) but approximately 4 cubic centimeters was the average amount. This corresponded to approximately 0.02 grams of sulfuric acid after conversion by the catalyst. This sulfur dioxide was evolved over a ten minute period and in a total volume of air of 1 liter, thus giving an average sulfuric acid concentration of about 2×10^{-5} grams per cubic centimater. This value is about 100 times that expected in exhaust gases from catalyst equipped cars.

2. Trapping of Sulfuric Acid

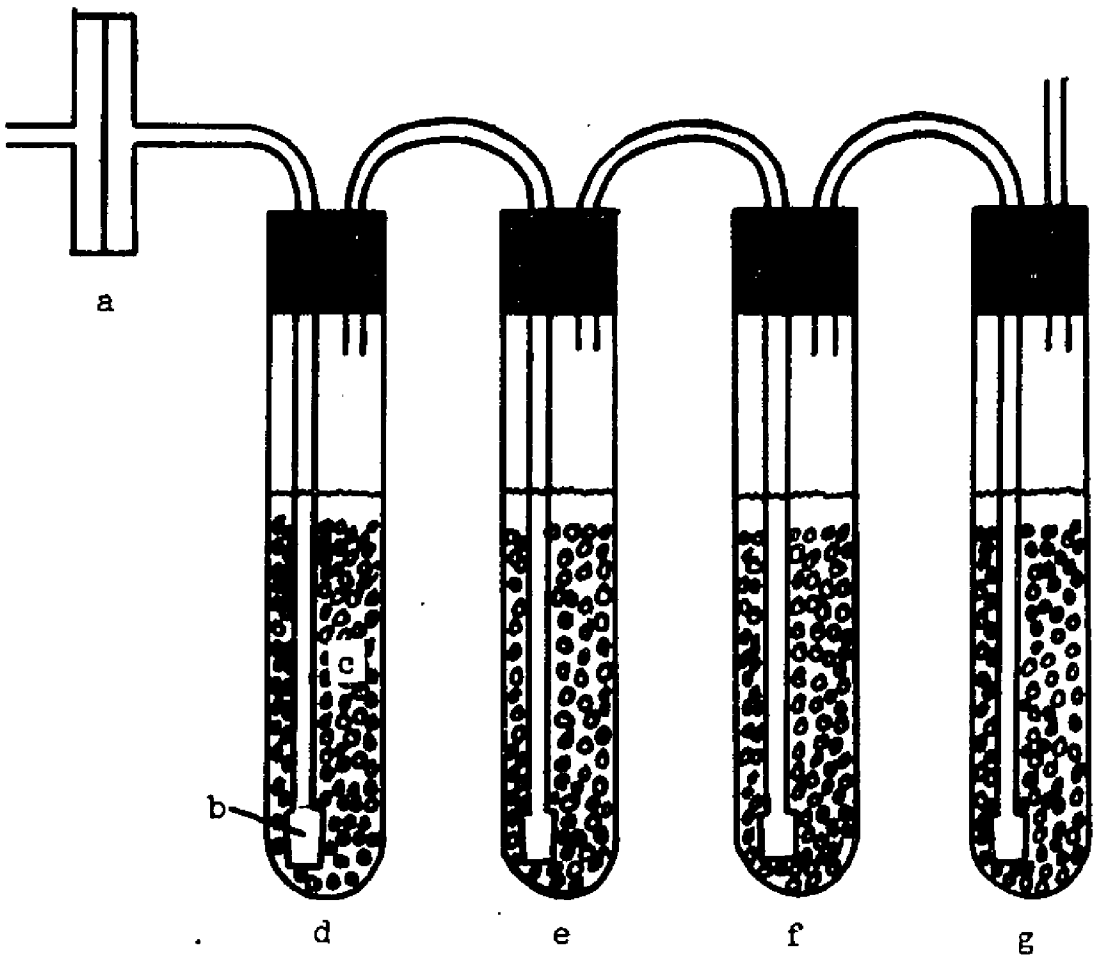
Except for the fluoropore filter, each of the traps consisted of 10 milliliters of 0.1 molar aqueous solution in a 20 x 150 millimeter test tube. Gas dispersion tubes and glass beads were used to maximize the contact of the gas with the trapping solution. The effluent from the catalyst was directed through the traps in the following order: sodium tetrachloromercurate(II), water, sodium carbonate, sodium hydroxide. Sodium tetrachloromercurate(II) is the sulfur dioxide-specific absorbing solution used in

the West-Gaeke test for sulfur dioxide. Its purpose as a trap was to remove any sulfur dioxide that passed through the catalyst unoxidized and thence through the filter, so that a correction for the amount of sulfuric acid generated could be made. As it turned out, the catalyst was essentially 100% efficient for the conversion of sulfur dioxide to sulfur trioxide and sulfuric acid at 400°C, as shown by the absence of sulfur dioxide in the sodium tetrachloromercurate(II) trap. The trapping arrangement is shown in Figure 17. The fluoropore filter was located 1½ feet from the catalyst.

3. Analysis of the Traps

Sulfur-35, with an 87 day half life, decays to chlorine-35 by emission of a 0.167 MeV beta particle. The low energy of this radiation required that liquid scintillation counting be the method of measuring the activity of the various solutions. Liquid scintillation cocktail consisting of 6 grams of 2,5-diphenyloxazole (PPO), 0.25 grams of 1,4-di-2(5-phenyl-oxazolyl)-benzene (POPOP), and 100 grams of naphthalene in a liter of p-dioxane was prepared and used for the counting medium.

One milliliter of solution was taken from the reaction vessel both before and after the reaction was per-



a. Fluoropore filter

b. Gas dispersion tube

c. Glass beads

d. Na_2HgCl_4 solution

e. H_2O

f. Na_2CO_3 solution

g. NaOH solution

Figure 17. SULFURIC ACID TRAPPING ARRANGEMENT

formed and was placed in a counting vial with 18 milliliters of cocktail. After the reaction, the fluoropore filter was placed totally in a counting vial with 18 milliliters of cocktail, and 1 milliliter from each of the traps was similarly treated. The volume of solution in each vial was increased to 20 milliliters by addition of distilled water to help solubilize the sample. The radioactivities of the solutions were then measured by the liquid scintillation counting technique with a counting time of 10 minutes for each sample. Quench correction factors were determined and applied for each of the solutions involved in the scintillation counting in order to normalize the data. The results are shown in Table 15.

It was thought that perhaps by moving the traps farther from the catalyst, more time would be given for the freshly generated sulfuric acid to coalesce and form larger droplets, thereby increasing its trappability. To see the effect of increased distance, the transfer line from the catalyst to the fluoropore filter was lengthened to 5 feet and the experiment repeated. The results are shown in Table 16.

4. Discussion and Conclusion

The data indicate that sulfuric acid, as freshly

TABLE 15

Radioactivities and Trapping Efficiencies

of the Various Sulfuric Acid Traps

(1½ Foot Transfer Line)

	cpm/ml sample	cpm/total solution*	% of trapped H_2SO_4**
Before reaction	4220.6	108385	
After reaction	3299.4	99509	
Filter	28.2	28.2	0.3
Na_2HgCl_4	47.6	500	5.6
H_2O	28.1	281	3.3
Na_2CO_3	445.4	4677	52.8
NaOH	321.1	3368	38.0

*Total activity lost = 8876 cpm

**Total activity trapped = 8854 cpm

TABLE 16

Radioactivities and Trapping Efficiencies

of the Various Sulfuric Acid Traps

(5 Foot Transfer Line)

	cpm/ml sample	cpm/total solution*	% of trapped H_2SO_4*
Before reaction	3790.3	95195	
After reaction	2803.3	85275	
Filter	81.0	81.0	0.8
Na_2HgCl_4	61.9	651	6.7
H_2O	42.0	420	4.3
Na_2CO_3	443.2	4740	48.7
NaOH	366.8	3850	39.5

*Total activity lost = 9920 cpm

**Total activity trapped = 9742 cpm

generated by platinum catalyst, is indeed difficult to trap. The fluoropore filter trapped less than 1% of the sulfuric acid and the water trapped less than 5%. The alkaline traps proved, as expected, to be the best and it was interesting to note that almost 40% of the sulfuric acid passed through the sodium carbonate trap.

Moving the traps to 5 feet from the catalyst resulted in an almost three-fold increase in the efficiency of the fluoropore filter but the percent of sulfuric acid trapped was still less than one. This increase, however, does indicate that the size of the droplets increased somewhat in the extended tube. In an automobile exhaust, some coalescence of the droplets may be expected and some increase in the efficiency of the fluoropore filter for trapping sulfuric acid may also occur. However, the concentration of sulfuric acid in the exhaust gases is considerably smaller than that employed in these studies and this should limit the extent of coalescence. The present data indicate that the efficiency of trapping will certainly not approach 100%.

It was concluded that trapping of freshly generated sulfuric acid is a very inefficient process and that data based on these techniques are probably erroneously low. These studies very clearly show the need for a measurement method for sulfuric acid which does not involve trapping.

B. Studies of Laser Induced Infrared Emission From Sulfuric Acid Aerosol

The overall aim of our research group has been the development of a remote sensing device for atmospheric pollutants utilizing laser induced phenomena. To this end, numerour studies have been conducted on various compounds which are considered pollutants. The primary phenomenon studied thus far has been laser induced infrared fluorescence. In order for a pollutant to interact with the radiation from the carbon dioxide laser which is used, the pollutant has to absorb radiation at the wave length of the laser beam (10.6 microns). Sulfuric acid was found to absorb infrared radiation strongly at 10.6 microns (Figure 18) thus suggesting that sulfuric acid might be excited by absorption of the laser beam and caused to emit characteristic radiation which could be used for its analysis.

1. Generation of Sulfuric Acid Aerosol

Sulfuric acid aerosol was generated by aspirating concentrated sulfuric acid through a Beckman atomizer-burner using nitrogen as the aspirator gas. No flame was used. The nitrogen flow rate was regulated with a Matheson 601 flow meter and studies were conducted on aerosols produced at nitrogen flow rates of 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5,

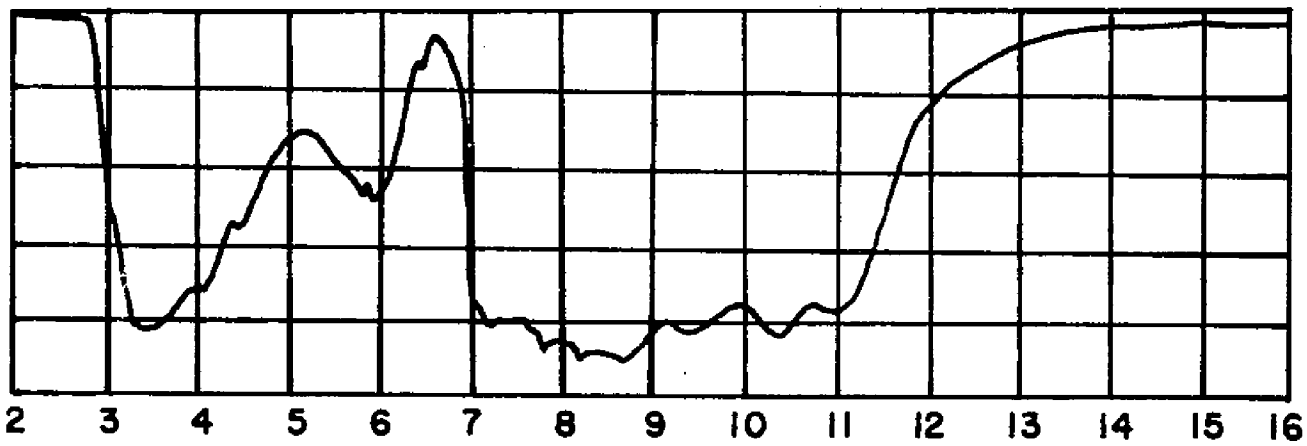


Figure 18. INFRARED ABSORPTION SPECTRUM OF 96% SULFURIC ACID

4.0, and 4.5 liters per minute. No aerosol particle size analysis was attempted.

2. Vibrational Excitation of Sulfuric Acid Aerosol

Initially, the excitation of the sulfuric acid aerosol was attempted at the maximum laser power of 30 watts and at various aspirator gas flow rates by simply aspirating the sulfuric acid downwards through the laser beam. This arrangement gave no emission signal from the sulfuric acid.

It was reasoned that the power density in the laser beam was too low for efficient excitation of the sulfuric acid. In order to increase the power density in the laser beam, a concave, front surface aluminum mirror with a 20 centimeter focal length was used to focus the beam such that the diameter of the focal point was 1 millimeter. The laser, mirror, and atomizer were positioned in such a way that the focal point of the beam was approximately 3 millimeters directly below the sulfuric acid outlet of the atomizer. The positioning was accomplished by placing a straight piece of nichrome wire in the atomizer outlet so that it projected straight down from the atomizer. The laser was then focussed onto the wire, which resulted in heating and glowing of the wire when positioning was correct. This actually served two purposes. It aided in focussing the laser beam

properly and also provided a light source at the intended point of sulfuric acid excitation, which was used in positioning the monochromator-detector system so that the emitted radiation could be focussed on the monochromator entrance slit by a collecting mirror. The focussing of the laser beam in the sulfuric acid aerosol from the atomizer did result in an emission signal from the excited acid and studies were then conducted using the focussed beam.

Using the experimental arrangement depicted in Figure 19, concentrated sulfuric acid was aspirated through the focal point of the laser beam and a portion of the emitted radiation was collected and focussed onto the entrance slit of the monochromator-detector system.

3. Analysis of the Emission from Excited Sulfuric Acid

A McPherson Model 218 monochromator, fitted with a McPherson 607 filter assembly and a Barnes Engineering Model 662 Triglycene Sulfate (TGS) pyroelectric detector, was used in all of the laser induced emission studies. The detector signals were amplified by a Princeton Applied Research Model 124 lock-in amplifier and displayed on a Texas Instruments Servo-Riter strip chart recorder. A Princeton Applied Research Model 125 mechanical chopper was used to modulate the emission signals at 13 Hertz just

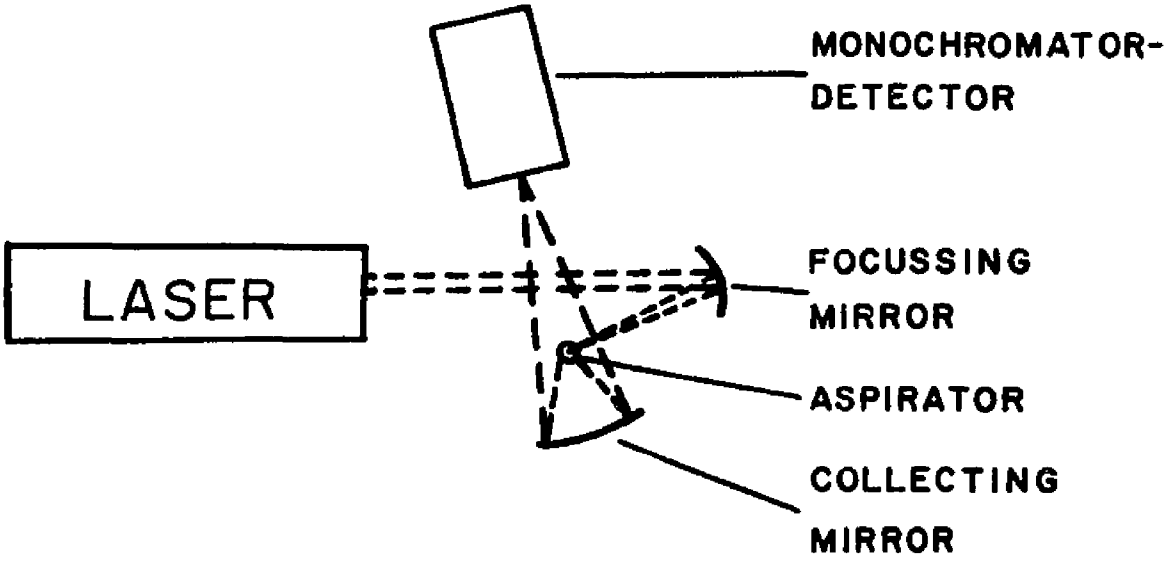


Figure 19. EXPERIMENTAL ARRANGEMENT FOR SULFURIC ACID INFRARED EMISSION STUDY

prior to entrance into the monochromator.

a. Collecting System

A concave, front surface aluminum mirror with a diameter of 10 centimeters and a focal length of 20 centimeters was used to collect a portion of the radiation emitted by the excited sulfuric acid and to focus it on the entrance slit of the McPherson monochromator. The positioning of this mirror was critical and little success with the experiment was realized until the nichrome wire was used as previously described.

b. Laser Induced and Thermal Spectra of Sulfuric Acid

With the optical system optimized, the sulfuric acid was aspirated wiyh an aspirator gas flow rate of 1 liter per minute, the laser was adjusted to its maximum power of 30 watts, and a laser induced infrared emission spectrum was obtained for sulfuric acid aerosol. The spectrum was scanned with the monochromator from 2 microns to 16 microns, and is shown in Figure 20.

For comparison purposes, the thermal emission spectrum of sulfuric acid was obtained by heating a small amount of sulfuric acid in a small nitrogen filled, pyrex glass cell fitted with an Irtran-2 window. The spectrum

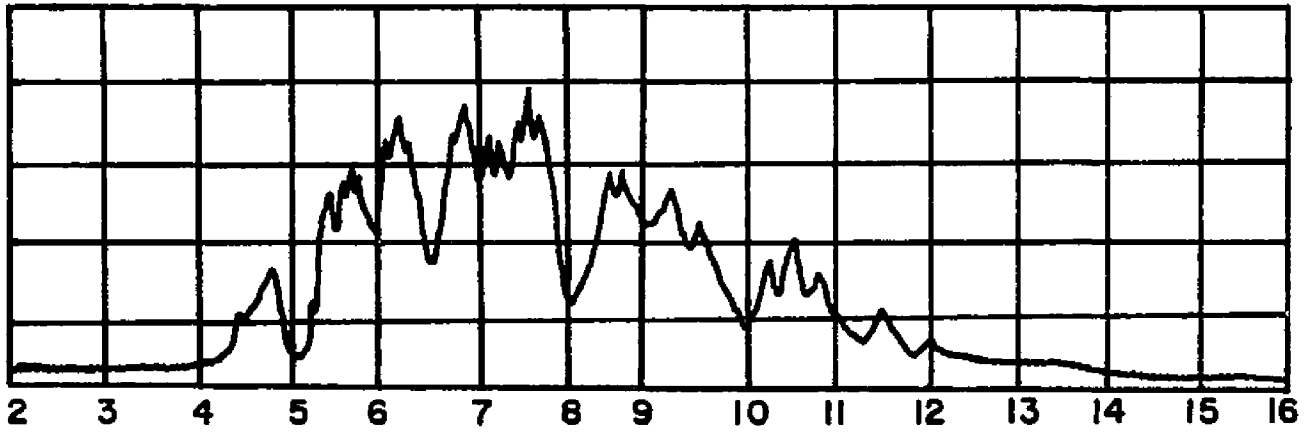


Figure 20. LASER INDUCED INFRARED EMISSION SPECTRUM OF 96% SULFURIC ACID

was scanned and recorded with a Beckman IR-10 infrared spectrophotometer. This spectrum is shown in Figure 21

The thermal emission spectrum and the laser induced spectrum were seen to be similar, but with significant differences. This indicated that the species giving rise to the spectra were not precisely the same. The exact nature of the laser excited system is not known, but the emission spectrum produced by it is reproducible and apparently characteristic.

c. Selection of a Wavelength for Monitoring

The laser induced emission spectrum was recorded primarily in order to select a characteristic emission band for monitoring. It was required that this band be in a region of the spectrum which would be relatively free from interferences from other excited compounds. The band centered at 6.27 microns was chosen. This is in a region of the spectrum where water might be expected to interfere, but aspiration of water into the laser focus gave no emission signal at this wavelength. Aromatic compounds might also be expected to interfere, but aromatics should not be present in exhaust gases from catalyst-equipped cars.

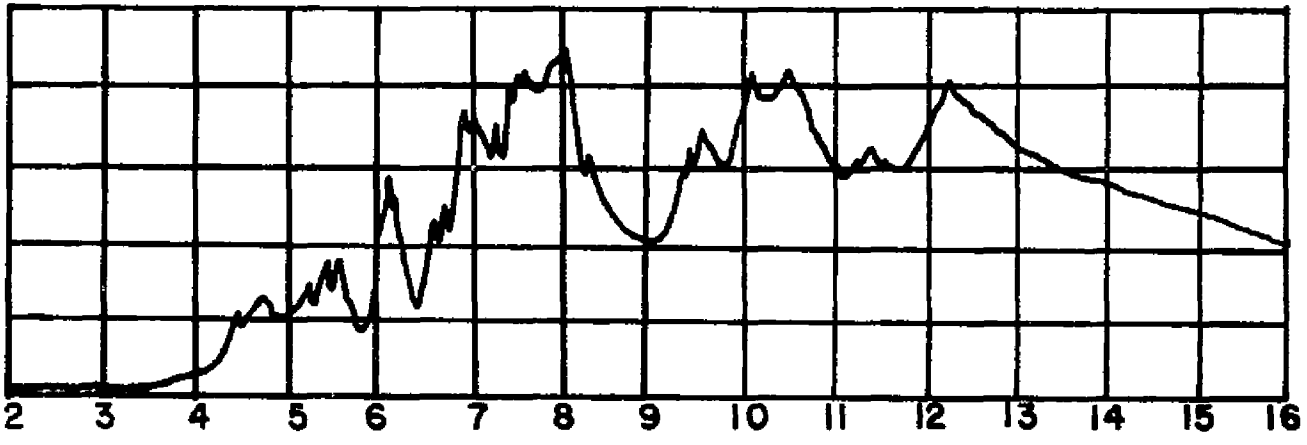


Figure 21. THERMAL EMISSION INFRARED SPECTRUM OF 96% SULFURIC ACID

4. Emission Intensity Versus Laser Power

The volume of vapor monitored was calculated to be 5×10^{-14} cubic centimeters. The calculation was made assuming the excitation zone to be a sphere within the laser focus, having a diameter equal to the diameter of the focal point.

The intensity of the emission signal from laser excited sulfuric acid at 6.27 microns was measured at aspiration rates of 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, and 4.5 liters per minute and at laser powers of 10, 15, 20, 25, and 30 watts. The laser powers are reported as the power of the unfocussed beam as measured by a Coherent Radiation Model 201 power meter interposed between the laser and the focussing mirror. The laser was normally adjusted to the desired power with the power meter in position in the beam, and then the irradiation of the sulfuric acid aerosol was accomplished by moving the power meter out of the beam. The interrelationship between emission signal intensity, aspirator gas flow rate, and laser power is shown in Figure 22. It can be seen that maximum signal was obtained at a flow rate of 1 liter per minute for all laser powers used and the signal intensity decreased rapidly at higher flow rates. It is revealing to note that laser powers of 25 and 30 watts both gave rise to the same signal intensity at a flow rate of 1 liter

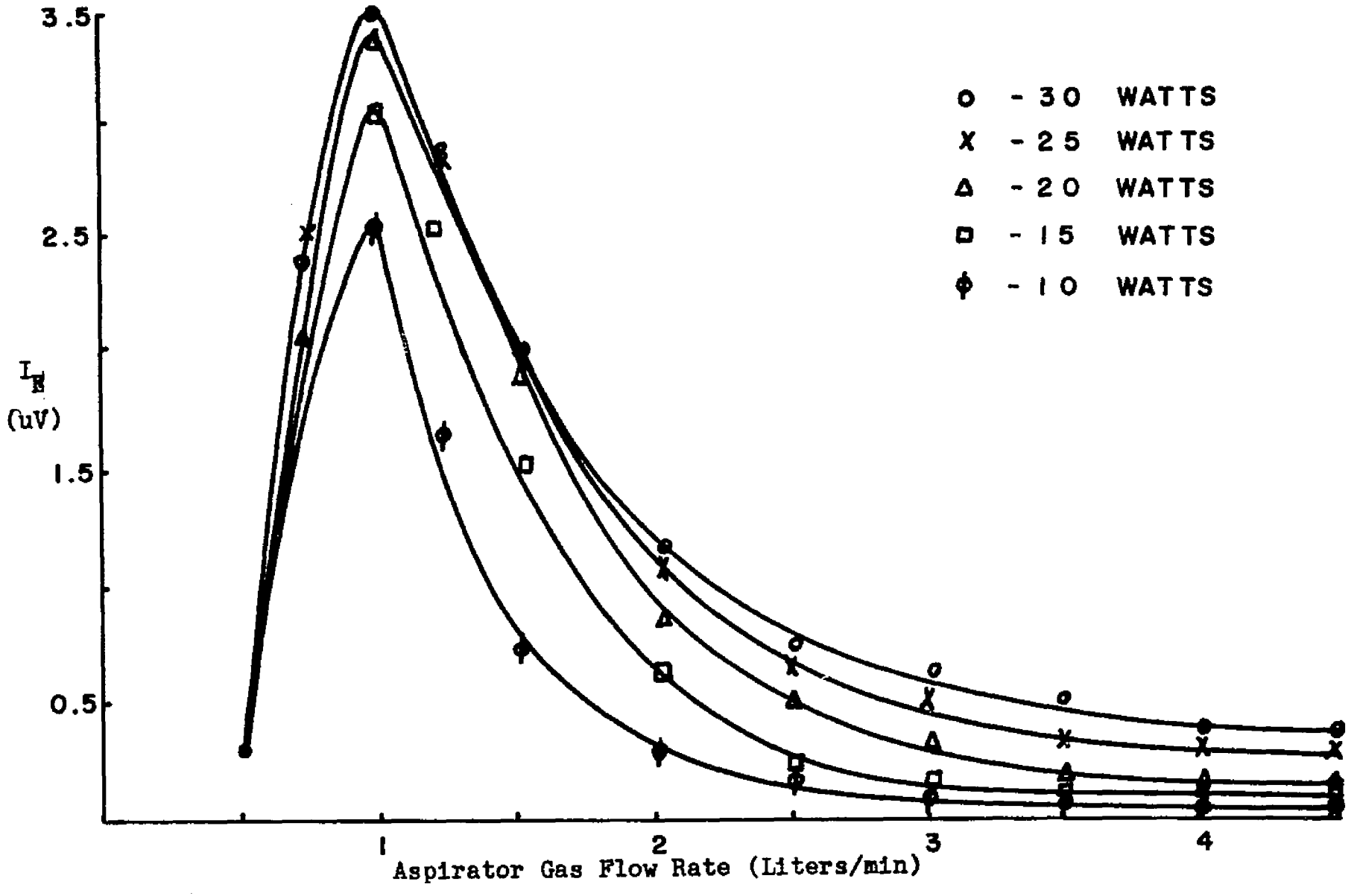


Figure 22. LASER INDUCED EMISSION OF SULFURIC ACID AT 6.27 MICRONS

per minute. This indicated that the sample remained within the focal sphere of the laser beam long enough so that all of the sulfuric acid became excited and emitted radiation. At this flow rate, the signal intensity was independent of laser powers greater than 25 watts when all the sample in a small volume was excited. At higher flow rates, the signal decreased for all laser powers used and a power effect was shown. This indicated that the sulfuric acid droplets moved through the laser focus too fast for complete excitation and emission even at 30 watts. The same data used in Figure 22 were plotted in a different fashion in Figure 23 to show more graphically the effect of laser power on emission intensity. At flow rates of 2.0 to 4.5 liters per minute, there was a linear relationship between signal intensity and laser power up to 30 watts.

It was seen, then, that for the system described, optimum operating conditions were achieved at an aspirator gas flow rate of 1 liter per minute and at laser powers greater than 25 watts. Under these conditions, the emission intensity was independent of laser power. At conditions other than optimum: emission intensity was proportional to laser power; emission intensity was inversely proportional to the gas flow rate; at flow rates greater than 2 liters per minute, emission intensity was linear with laser power.

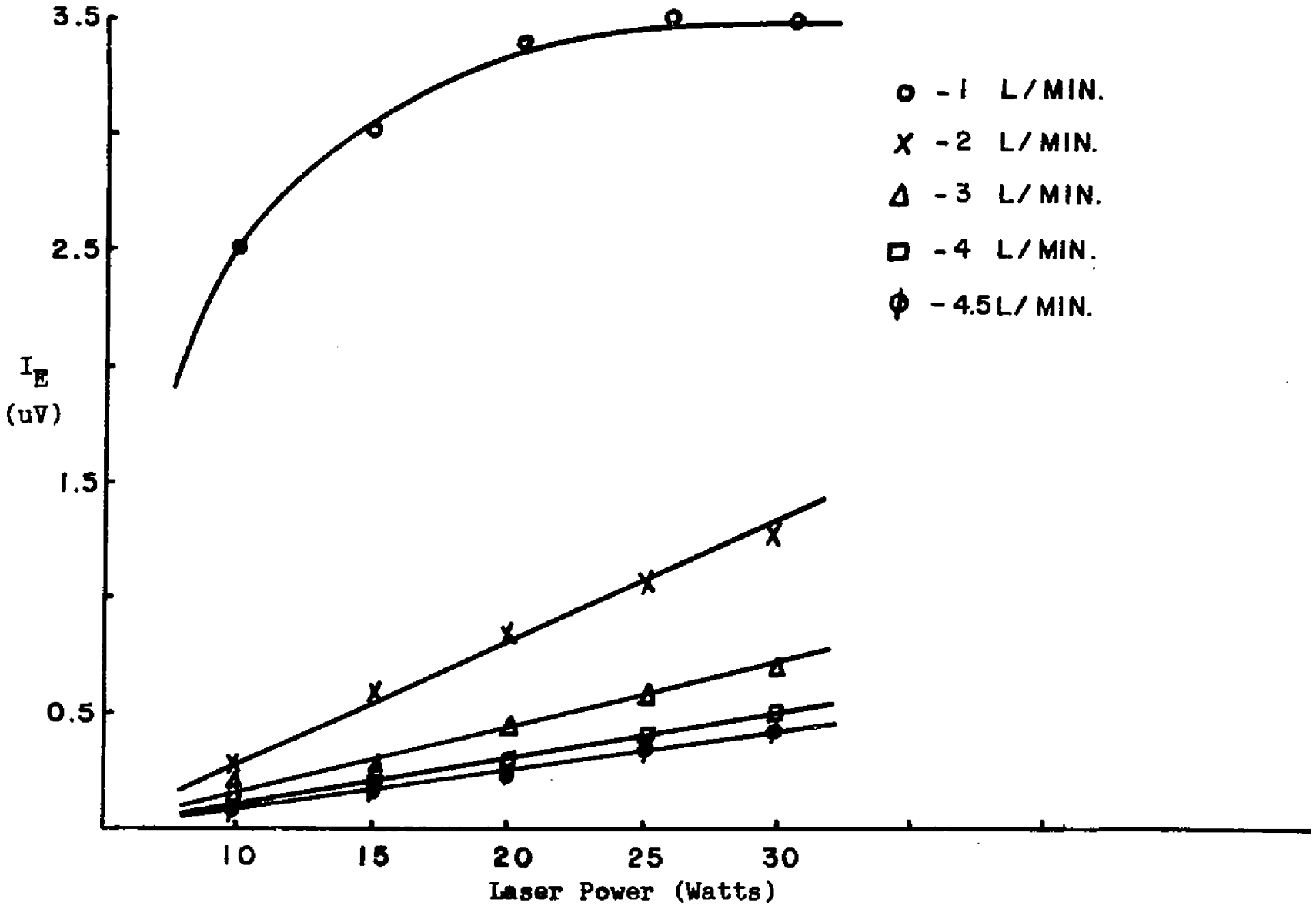


Figure 23. LASER INDUCED EMISSION OF SULFURIC ACID AT 6.27 MICRONS

5. Analytical Sensitivity

In order to determine the sulfuric acid flow rate at optimum conditions, the sulfuric acid was aspirated at 1 liter per minute into a tared container for 5 minutes. The container was then weighed again and the weight of sulfuric acid present was determined. Division by 5 minutes gave the flow rate. Using the emission signal data obtained under optimum conditions and the measured sulfuric acid flow rate, the sensitivity data shown in Table 17 were calculated. In calculating the absolute sensitivity, it was assumed that a recorder pen deflection of 3 recorder chart units above the background signal could reasonably be detected. The maximum pen deflection under optimum conditions was 70 units and the background signal was 2 units.

Assuming 100% efficiency for the conversion of sulfur dioxide to sulfuric acid by the automotive catalytic converter and assuming an average sulfur content of 0.03% for gasoline, the concentration of sulfuric acid in the exhaust gases would be on the order of 10^{-7} grams per cubic centimeter. The calculated sensitivity for the laser induced infrared emission technique was approximately 10^{-6} grams per cubic centimeter, which is one order of magnitude below that which is needed for measuring the concentration of sulfuric acid aerosol in automobile gases. These data

TABLE 17

Analytical Sensitivity of Laser Technique For Determining Sulfuric Acid

Volume Monitored	5×10^{-4} cc
Nitrogen Flow Rate	1 liter/min.
H_2SO_4 Flow Rate	0.03 g/min.
Weight of H_2SO_4 In Monitored Volume	2×10^{-8} g.
Signal	3.5 uV
Sensitivity (Absolute)	1×10^{-9} g.
Sensitivity (g/cc)	2×10^{-6} g/cc

do indicate, however, that the method is feasible and further study and improvements in the system could easily bring the sensitivity to that required for monitoring of automobile exhausts.

IV. GENERAL DISCUSSION AND CONCLUSIONS

PART I

The several reasons for the performance of this research have been stated. The initial interest was whether the reaction of propylene was fast enough to be a source of analytical interference in the remote sensing of propylene by laser induced infrared fluorescence. The uniqueness of the reactions under the influence of the relatively low power, continuous infrared laser beam provided the impetus for the second phase of the research. This phase was concerned with the characterization of the products resulting from the reaction of propylene under varying conditions of laser power and oxygen concentration. In association with this study, an increase in temperature was noted with the absorption of the laser beam. A study was undertaken to evaluate the relationship of this increase in thermal energy to the reaction. The final study was undertaken in an effort to gain insight into the nature of the laser induced propylene - oxygen reaction.

The laser induced reaction of propylene was noted as a side effect during a laser induced infrared fluorescence experiment. The overall aim of the fluorescence research was the development of a remote sensing device for

atmospheric pollutants. The process is conceived as consisting of an infrared laser beam being swept through a region of the atmosphere and an optical system for gathering of the induced fluorescence from the pollutants. The movement of the laser beam and the movement of air currents is seen as limiting the period of exposure of the pollutant to the laser beam to a few seconds. The reaction of propylene induced by exposure to the laser radiation was determined to be too slow to cause a significant decrease in the concentration of propylene during the time required for a fluorescence measurement. The reaction of propylene, then, is not considered a major cause of analytical interference in remote sensing experiments.

The chacterization of the products from the propylene - oxygen reaction indicated a dependence of the reaction on both laser power and oxygen concentration. Studies were conducted with laser powers of 20 and 35 watts and with several propylene - oxygen mixtures. No studies were performed with concentrations inside the flammability limits of propylene because of the danger of explosion.

In the early stages of the work utilizing the large reaction cells, high molecular weight alkanes were produced in small quantities from a very slow reaction. This was a result which was different from all subsequent

studies. NMR analysis indicated an average degree of branching which was considerably less than that given by the $\left[-CH_2-\underset{CH_3}{CH}-\right]$ repeating unit of polypropylene. It was concluded therefore, that a straightforward free radical polymerization of propylene did not occur. The exact nature of the reaction remains unclear, although later studies indicated the presence of numerous free radicals, including triplet methylene, which could conceivably account for the reaction products. The absence of the lower molecular weight products which were seen in later studies with the smaller cells was concluded to be due to the low yield of products and the large volume of the cell, both of which contributed to the formation of concentrations too small to detect.

With low laser beam power (20 watts) and utilizing the smaller, 18 centimeter cell, propylene alone did not react. The amount of energy absorbed was insufficient to cause any bond cleavage. Mixtures of 90% propylene - 10% oxygen and 70% propylene - 30% oxygen, however, did react, making it obvious that oxygen was necessary for a reaction to take place. The extent of reaction increased from 0.1% conversion of propylene to 4% conversion with an increase of the oxygen concentration from 10% to 30%. In both cases acetaldehyde was the major product, with it constituting

98.6% of the products in the 10% oxygen reaction and 65.3% in the 30% oxygen reaction. It was concluded that the acetaldehyde was an initial product of the interaction of propylene with oxygen (Later results indicated that formaldehyde was also probably an initial product.) and that, at 20 watts, the reaction essentially stopped at that stage.

At higher laser beam power (35 watts), propylene did not react when oxygen was scrupulously excluded. Previously, propylene had always reacted but oxygenated products had always been present. The lack of reaction in the true absence of oxygen showed conclusively that bond scission in the propylene did not take place as a result of direct absorption of the laser radiation. As previously stated, the breakage of the pi bond in propylene would require the absorption of 25 photons of 10.6 micron radiation per molecule. The breakage of the total carbon-carbon double bond would require the absorption of 52 photons per molecule. Obviously these were doubtful possibilities, but they had to be considered as possibilities until the present data were obtained.

As with the low power irradiation, mixtures of 90% propylene - 10% oxygen and 70% propylene - 30% oxygen did react when exposed to 35 watt laser radiation. The extent of reaction at the higher power was much greater,

however. 90% propylene - 10% oxygen gave 16% conversion to products and 70% propylene - 30% oxygen gave 27% conversion, showing a continuing dependence on oxygen concentration. The gaseous product distributions at high laser beam power, while similar for the 10 and 30% oxygen concentrations, were considerably different from those obtained when low laser power was used. Notably, the acetaldehyde concentration in the products decreased to approximately 30%. There also appeared a number of products that had not previously been detected in any reaction mixture. These data suggested that, as with the 20 watt irradiations, acetaldehyde was formed as an initial product but, under the influence of the higher power, it further reacted to form the additional products. Analysis of the liquid products from the 70% propylene - 30% oxygen reaction showed additional products not previously detected. The presence of formaldehyde in the mixture was viewed as important with respect to a possible mechanism for the initial interaction of propylene with oxygen. The absence of the high molecular weight products obtained in the large cell is not understood.

The absorption of the laser beam by propylene and by the Irtran windows caused an increase in the temperature as previously noted. The study performed by thermally heating a mixture of 90% propylene and 10% oxygen to 200^{o}C for

1 hour showed no reaction products and it was concluded that the laser induced reactions were not primarily thermal in nature.

The final studies, undertaken to gain insight into the nature of the laser induced propylene - oxygen reaction, were directed towards the determining of the role of acetaldehyde in the reaction. As previously noted, irradiation of acetaldehyde gave a product distribution which was in good agreement with that obtained by Laidler and Liu[37] for the thermal decomposition of acetaldehyde at 523°C. In the mechanism proposed by Laidler and Liu and shown on page 80, numerous free radicals are proposed as being formed in the reaction. The formation of these free radicals in the propylene - oxygen reaction would adequately explain the formation of all of the observed products except ethylene, 2-butene, and 4-methyl-1,3-dioxolane.

The vibrational frequency which corresponds to the 10.6 micron absorption band in acetaldehyde is assigned to a CH_3 rocking motion.[45] Although the temperature within the cell during a laser induced reaction is far below the temperature required for thermal decomposition of acetaldehyde, there is the possibility that a laser induced non-Boltzman distribution over the allowed vibrational states exists. Such a perturbed distribution could easily give a ratio of

populations in the first excited and ground vibrational states, for the CH_3 rocking motion, equal to or greater than that for a Boltzman distribution at 523°C. The effect of such a perturbation on the reaction rate could be such that the decomposition reaction would occur at a much lower temperature than possible in the absence of laser radiation. It has been shown that absorption of radiation from a laser by a molecule can lower the energy of actibation for a given reaction.[24]

The 90% acetaldehyde - 10% oxygen laser induced reaction resulted in the formation of acetic acid along with the other products shown in Table 10. The significance of the formation of acetic acid lies in the fact that acetic acid is known to decompose thermally forming ketene and ethylene and several other products.[38] Both acetic acid and ketene absorb infrared radiation at 10.6 microns and ketene is known to decompose both thermally and photolytically to form methylene.[40] The formation of methylene in the reaction between propylene and pxygen would explain the formation of all of the products not explained by the Laidler and Liu scheme.

The reaction of 90% propylene and 10% acetaldehyde to form methane, carbon monoxide, ethylene, ethane, 1-butene, and a hexadiene showed convincingly that the acetaldehyde

does indeed react with propylene under the influence of the laser to give a number of the products previously seen in the propylene - oxygen reaction. Addition of a small amount of oxygen to this system resulted in the formation of the same products observed in the propylene - oxygen reaction.

An experiment utilizing 1,3-butadiene as a trapping agent resulted in the formation of cyclopentene as one of the products. This was an indication of the formation of triplet methylene when acetaldehyde was irradiated with the laser beam.

It was concluded that propylene interacts with oxygen initially to form acetaldehyde and formaldehyde - probably through a 1,2-dioxetane intermediate. The acetaldehyde then reacts through a free radical mechanism, and through the formation of acetic acid and its subsequent decomposition to form reactive species which adequately account for the observed products in the propylene - oxygen reactions.

PART II

The primary impetus for the research herein described was the need for a good, reliable, specific test for sulfuric acid aerosol. This need was brought into focus by the discovery that the catalytic converters which were being installed in new cars produced sulfuric acid in the exhaust gases. There has been a good deal of concern generated over exactly how much sulfuric acid is being generated and what is the likely health effect of these emissions. The various procedures that have been used for exhaust monitoring have produced different results.[30] All of these methods in use thus far have utilized trapping techniques and involve analysis for sulfate. All of the data that have been released thus far on sulfuric acid aerosol emission levels in catalyst-equipped car exhausts have been estimates based on inconsistent results from these questionable techniques.

One of the most widely used trapping agents is 0.5 micron pore size fluoropore filter material. The research reported here indicated that the fluoropore filter material does not efficiently trap freshly generated sulfuric acid, as generated from sulfur dioxide by heated platinum catalyst. The research, in fact, showed that freshly generated sulfuric acid is quite difficult to trap in general. This pointed to the need for a measurement technique for

sulfuric acid aerosol which does not involve trapping at all.

The laser induced emission study showed that the determination of sulfuric acid aerosol by laser induced infrared emission is indeed feasible. The calculated sensitivity for the laboratory system of 2×10^{-6} grams per cubic centimeter is below that which is calculated as being necessary for automobile exhaust monitoring. However, it is projected that, with increased laser power, the volume of sample which is excited by the laser could be greatly enlarged and the same power density necessary for complete excitation of the sulfuric acid maintained. For example, assuming a continuing linear relationship between emission intensity and laser power, an increase in the diameter of the focal sphere to 2 millimeters with the same power density would result in an increase in the sensitivity to 2×10^{-7} grams per cubic centimeter, which is the order necessary for automobile exhaust monitoring. With sufficient laser power, focussing of the laser beam might not be necessary at all, thereby greatly increasing the volume of sulfuric acid being monitored.

Because of the many variables involved in automobile exhayst systems, it is unsafe to predict, based on these preliminary data, what laser power would be necessary to produce a routine instrument. Experimental results show,

however, the technique to be promising. It offers the possibility of measuring the sulfuric acid aerosol specifically, with no complicating interferences. It also offers the possibility of measuring sulfuric acid aerosol in situ, thereby eliminating the problems of collection and separation.

REFERENCES

1. G. Grau, Laser, Edited by W. Kleen and R. Muller (Springer-Verlag, Berlin, 1969), pp. 510-556.
2. W.J. Jones, Quart. Rev., 23, 73 (1969).
3. A.F. Haught, Ann. Rev. Phys. Chem., 19, 343 (1968).
4. B. Chu, Ann. Rev. Phys. Chem., 21, 145 (1970).
5. J.W. Robinson, C. Woodward, and H.M. Barnes, Anal. Chim. Acta, 43, 119 (1968).
6. J.W. Robinson, H.M. Barnes, and D.M. Hailey, Talanta, 16, 1109 (1969).
7. J.W. Robinson, D.M. Hailey, and H.M. Barnes, Anal. Chim. Acta, 56, 175 (1971).
8. J.W. Robinson and J.L. Guagliardo, Spec. Letters, 6, 271 (1973).
9. G.B. Morgan, G. Ozolins, and E.C. Tabor, Science, 170, 289 (1970).
10. W. Leithe, The Analysis of Air Pollutants, (Ann Arbor Humphrey Science Publishers, Ann Arbor, 1970) pp. 226-263.
11. R.T.H. Collis, Appl. Opt., 9, 1782 (1970).
12. H. Kildal and R.L. Byer, Proc. IEEE, 59, 1644 (1971).
13. James D. Dake, Analytical Parameters In The Remote Sensing of Air Pollutants Using Laser Induced Infrared

Fluorescence, Dissertation, Louisiana State University, 1973.

14. Paul J. Moses, Reactions of Ethylene Induced by CO_2 Laser Radiation, Dissertation, Louisiana State University, 1973.

15. C. Borde, A. Henry, and L. Henry, Compt. Rend. Acad. Sci. Paris, Ser. B, 263, 619 (1966).

16. C. Borde, C. Cohen, and L. Henry, Compt. Rend. Acad. Sci. Paris, Ser. B. 265, 267 (1967).

17. E. Quel and X. DeHemptinne, Ann. Soc. Sci. Bruxelles, Ser. 1, 83, 262 (1969).

18. P. Goerlich and L. Blankenburg, Exp. Tech. Phys., 17, 105 (1969).

19. R.M. Wilson, Ann. N.Y. Acad. Sci., 168, 615 (1970).

20. J. Bell, R.V. Edwards, B.R. Nott, and J.C. Argus, Ind. Eng. Chem. Fundam., Vol. 13, No. 1, 89 (1974)

21. M.W. Travers, Compt. Rend., 197, 1042 (1933).

22. N. Katayama, Interference Effects of Selected Compounds on the Determination of Ethylene in the Air by Laser Induced Infrared Fluorescence, Dissertation, Louisiana State University, 1974.

23. M.W. Travers, op. cit.

24. M.F. Goodman, H.H. Seliger, and J.M. Minkowski, Photochem. Photobiol., 12, 355 (1970).

25. F. Leh and K.M. Chan, J. Chem. Ed., 50, 246 (1973).

26. R.E. Walker, A.G.F. Brooks, and J. Cartwright, Int. J. Air and Water Pollut., 7, 773 (1963).

27. E.R. Allen, R.D. McQuigg, and R.D. Cadle, Chemosphere, 1, 25 (1972).

28. P. Urone and W.H. Schroeder, Environ. Sci. Tech., 3, 436 (1969).

29. Trent R. Lewis, Archives Env. Health, V26, N1, P16 (6) (1972).

30. Russel E. Train, Before the Committee on Public Works of the United States Senate, Nov. 6, 1973.

31. B.T. Commins, Analyst, 88, 364 (1963).

32. J.F. Roesler, J.J.R. Stevenson, and J.S. Nadar, J. Air Pollut. Contr. Assoc., 15, 576 (1965).

33. P.W. West, A.D. Shendrikar, and Nicholas Herrara, Anal. Chim. Acta, 69, 111, (1974).

34. J. Kendall, Smith's Inorganic Chemistry, (C. Bell and Sons, Ltd., London, 1937) p. 419.

35. J.L. Guagliardo, A Feasibility Study of Ozone Remote Sensing by Laser Induced Infrared Fluorescence, Dissertation, Louisiana State University, 1973.

36. E. Stenhage, S. Abrahamson, and F.W. McLafferty, Atlas of Mass Spectral Data, (Interscience Publishers, New York, 1969)

37. K.J. Laidler and M.T.H. Liu, Proc. Roy. Soc., Ser. A, 297, 1450, 365 (1967).

38. F.O. Rice and K.R. Herzfeld, J. Amer. Chem. Soc., 56, 284 (1934).

39. C.H. Bamford and M.J.S. Dewar, J. Chem. Soc., 2877 (1949).

40. J. Hine, Divalent Carbon, (The Ronald Press Co., New York, 1964) p. 12.

41. W. Kirmse, Carbene Chemistry, (2nd Ed., Academic Press, New York, 1971) p. 209.

42. T.L. Gilcyrist and C.W. Rees, Carbenes, Nitrenes, and Arynes, (Thomas Nelson and Sons, Camden, New Jersey, 1969) p.59.

43. E.S. Corner and R.N. Pease, J. Amer Chem. Soc., 67, 2067 (1945).

44. P.W. West and G.C. Gaeke, Anal Chem., Vol. 28, No. 12, 1816 (1956).

45. K.S. Pitzer and W. Weltner, J. Amer. Chem. Soc., 71, 2842 (1949)

VITA

William Morris Reid was born December 14, 1939 in Meridian, Mississippi. He attended public elementary and junior high schools in Meridian, and graduated from Baton Rouge High School in Baton Rouge, Louisiana in May, 1957. In September, 1957, he entered Louisiana State University where he attended for two years. After an additional two years of working, he entered Northwestern State College of Louisiana where he received a B.S. degree in Education in August, 1964. He taught high school chemistry in Beeville, Texas for 3 years and then entered the University of Northern Iowa in September, 1967, where he attended on a National Science Foundation grant. He received an M.A. degree in Chemistry from that institution in August, 1968. After receiving the M.A. degree, he taught college chemistry at Bee County College for 4 years, and attended graduate classes at Louisiana State University each summer. In June, 1972, he entered graduate school at Louisiana State University for full time study and is currently a candidate for the degree of Doctor of Philosophy from this University. He is married to the former Frances Lowanda Leggett and they have two daughters.

EXAMINATION AND THESIS REPORT

Candidate: William Morris Reid

Major Field: Chemistry

Title of Thesis: Laser Induced Reactions of Propylene and A Study of the Feasibility of Determining Sulfuric Acid Aerosol by Laser Induced Infrared Emission

Approved:

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

Date of Examination:

November 25, 1974